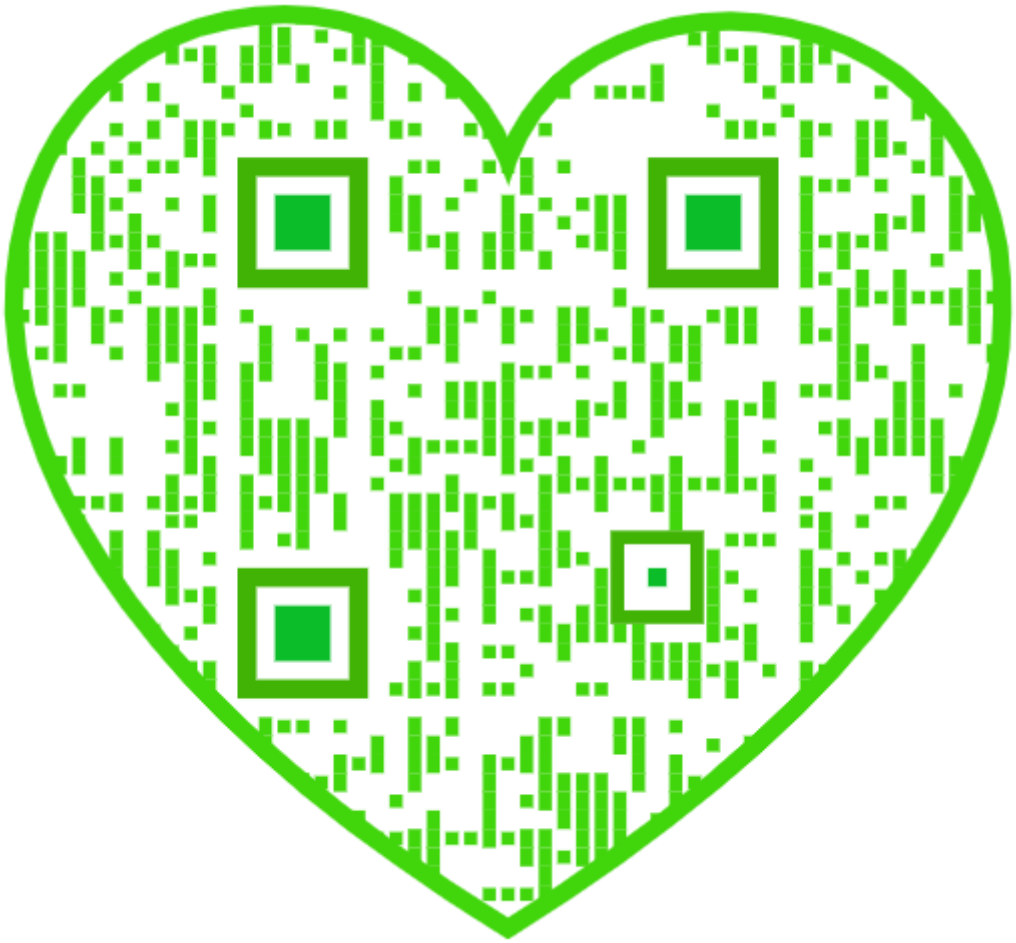

# PRACTICAL DENTAL METALLURGY

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# PRACTICAL DENTAL METALLURGY

A Text and Reference Book for Students and Practitioners of Dentistry

Embodying the Principles of Metallurgy, and Their Application to Dentistry, Including Experiments

BY

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*FIFTH EDITION—COMPLETELY REVISED*

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C. V. MOSBY COMPANY
1921

TO

THE MEMORY OF

**Clarke La Motte Goddard, A. M., D. D. S.,**

LATE PROFESSOR OF ORTHODONTIA,
DENTAL DEPARTMENT, UNIVERSITY OF CALIFORNIA

**This Work is Inscribed**

IN

ADMIRATION OF HIS TALENTS,

AND

GRATITUDE FOR HIS TEACHINGS, CRITICISMS
AND FRIENDSHIP

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## PREFACE TO FIFTH EDITION

At no time in the past, in so far as we have accurate knowledge of the past, has science proven to be of such great value to the world as now. Chemistry and metallurgy have shared with surgery, pathology, mechanics, engineering, and photography, the distinction of being necessary to world progress.

Every person should possess some knowledge of chemistry. The specialist demands a much broader acquaintance with the particular branch of chemistry which concerns his work if he would choose to be of service to his nation. So varied are the problems which depend upon a knowledge of chemical science for their solution, so limitless are the sources of this knowledge, that the average individual must depend upon the reading and study selected for him if he is to obtain but a fair knowledge of its application in his daily life.

In conformity with this idea and knowing that the exactness of science precludes any alteration of facts, the revision of this edition has been made with the view of eliminating obsolete methods of procedure and application and incorporating more recent methods in metallurgy in its application to dentistry or as a basic problem, and yet the fundamental instruction and the pedagogical scheme of the author have been carefully preserved. In a subject of this character the substance is not fully understood without the experimental work and as a result the two have been coupled.

The formation of the four year course in dental schools may give dental metallurgy a different place in

the curriculum. It is hoped that no less, but rather more time will be devoted to its study under these new conditions.

In this revision, the more important dental, chemical, and metallurgical journals have been consulted together with other reliable sources of information, for which due credit is given. Association with chemists has broadened our view, and teaching experience has made it possible to add much of interest to the subject which can not be incorporated in the text. Teachers are urged to add collections of stereopticon views of the mining and metallurgical industry, to add interest in a cultural way to the subject. In the end, a knowledge of metallurgy as applied to dentistry is the object sought, and it is hoped that this book may be an aid in imparting such knowledge to those for whom it is intended.

GUY S. MILLBERRY.

San Francisco, Cal.
September 1, 1918.

## PREFACE TO FOURTH EDITION

In this edition no effort has been made to change the pedagogic scheme of the author, which has received the endorsement of the teachers in the profession both by personal expression and by the adoption of the text in many of the dental schools since 1897. The subject matter, however, has been thoroughly revised in harmony with the latest information obtainable.

In order to avoid confusion in the mind of the student, the metric system has been used exclusively, all other sys-

tems of weights, measures and temperature having been eliminated, except the troy system in its application to precious metals, as any reform in this regard is obviously impractical.

Data for this revision have been gathered from all sources, including the more recent works on chemistry and metallurgy, but the bulk of the matter has been obtained from the journals of the American Chemical Society. Wherever possible, full credit has been given for all abstracts.

The pleasure of an intimate friendship with the author, first as a student and later as an associate in teaching, permits me to confirm the prevailing opinion of his qualifications as a teacher, and I trust his work may continue to merit the success which has previously been accorded it.

GUY S. MILLBERRY.

San Francisco, Cal.
September, 1911.

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## FROM PREFACE TO FIRST EDITION

In presenting this little volume to the practitioner and student of the dental profession, the author does not flatter himself that he is filling a void in such literature, or that a crying need has been felt in the profession for this particular production. It has, however, grown out of the exigencies of the writer's own class-room and laboratory after several years' practical experience as an instructor on its subject.

The endeavor has not been to furnish a scientific and exhaustive treatise on metallurgy, but rather to present, in a clear and practical manner, the principles of that subject as the author sees them related and applicable to the every-day wants of the dentist.

Keenly appreciating the reluctance with which this and the analogous study of chemistry have been pursued by the average student, the author has sought to awaken a deserving interest by doing away with the usual lectures and employing the work as a text book, subject to explanatory elaboration during the recitation; and to further make it so practical that it may be taken into the metallurgical laboratory and used as a manual for practical and experimental work. It presupposes the student to possess a fair knowledge of the principles of inorganic chemistry, comprehending the reading and writing of formulae, atomic affinities, and the expression of equations.

JOSEPH D. HODGEN.

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# PRACTICAL DENTAL METALLURGY

## CHAPTER I

## INTRODUCTION

**CHEMISTRY is that branch of science which treats of the atomic conditions of matter, and especially of atomic changes.** It comprehends the combination of diverse forms of matter producing new compounds, and the separating of already existing compounds into simpler ones, or resolving them into their ultimate principles, which are called—

**ELEMENTS.—Substances whose molecules contain one kind of atoms only,** and which all physical or chemical processes have as yet failed to break up or decompose into two or more dissimilar substances. It is not asserted that these substances are absolutely simple or elementary, or that they may not be found hereafter to yield more than one kind of matter, but merely so far as our knowledge extends it is so.

**Eighty-three elements** are at present known to us, of which the following is a partial list, arranged according to their electro-positive and -negative quality, or the electrochemical series. The most important are distinguished in the table by capitals, while those which at present are of slight importance, on account of their rare occurrence, or of our insufficient knowledge of their properties, are given in italics.

## TABLE OF ELEMENTS

| Symbol | | NEGATIVE END<br>Name | Valence | Atomic Weight† |
|---|---|---|---|---|
| O | | OXYGEN | II | 16.00 |
| S | | SULPHUR | II, IV, VI | 32.06 |
| N | | NITROGEN | I, III, V | 14.01 |
| F | | FLUORINE | I | 19.00 |
| Cl | | CHLORINE | I, III, V, VII | 35.46 |
| Br | | BROMINE | I, III, V, VII | 79.92 |
| I | | IODINE | I, III, V, VII | 126.92 |
| Se | | Selenium | II, IV, VI | 79.2 |
| P | | PHOSPHORUS | III, V | 31.04 |
| As | * | ARSENICUM | III, V | 74.96 |
| Cr | * | CHROMIUM | II, $(Cr_2)^{VI}$, VI | 52.0 |
| V | * | *Vanadium* | III, V | 51.0 |
| Mo | * | *Molybdenum* | II, IV, VI | 96.0 |
| W | * | *Tungsten* (Wolfram) | II, IV, VI | 184.0 |
| B | | BORON | III | 11.0 |
| C | | CARBON | IV | 12.0 |
| Sb | * | ANTIMONY (Stibium) | III, V | 120.2 |
| Te | | *Tellurium* | II, IV, VI | 127.5 |
| Ta | * | *Tantalum* | III, VI | 181.5 |
| Cb | * | *Columbium* (Niobium) | III, V | 93.1 |
| Ti | * | *Titanium* | IV | 48.1 |
| Si | | SILICON | IV | 28.3 |
| **H** | | **HYDROGEN** | I | 1.008 |
| Au | * | GOLD (Aurum) | I, III | 197.2 |
| OS | * | Osmium | II, IV, VI, VIII | 190.9 |
| Ir | * | Iridium | II, IV | 193.1 |
| Pt | * | PLATINUM | II, IV | 195.2 |
| Rh | * | *Rhodium* | II, IV | 102.9 |
| Ru | * | *Ruthenium* | II, IV, VI, VIII | 101.7 |
| Pd | * | Palladium | II, IV | 106.7 |
| Hg | * | MERCURY (Hydrargyrum) | II, $(Hg_2)^{II}$ | 200.6 |
| Ag | * | Silver (Argentum) | I | 107.88 |
| Cu | * | COPPER (CUPRUM) | II, $(Cu_2)^{II}$ | 63.57 |

TABLE OF ELEMENTS—CONT'D

| Symbol | | NEGATIVE END<br>Name | Valence | Atomic Weight† |
|---|---|---|---|---|
| U | * | *Uranium* | II, IV, VI | 238.2 |
| Bi | * | BISMUTH | III, V | 208.0 |
| Sn | * | TIN (Stannum) | II, IV | 118.7 |
| In | * | Indium | III | 114.8 |
| Pb | * | LEAD (Plumbum) | II, IV | 207.2 |
| Cd | * | CADMIUM | II | 112.4 |
| Tl | * | Thallium | I, III | 204.0 |
| Co | * | COBALT | II, $(Co_2)^{VI}$ | 58.97 |
| Ni | * | NICKEL | II, $(Ni_2)^{VI}$ | 58.68 |
| Fe | * | IRON (Ferrum) | II, VI, $(Fe_2)^{VI}$ | 55.84 |
| Zn | * | ZINC | II | 65.37 |
| Ga | * | Gallium | $(Ga_2)^{VI}$ | 69.9 |
| Mn | * | MANGANESIUM | II, IV, VI, VIII | 54.93 |
| La | * | *Lanthanum* | III | 139.0 |
| Ce | * | Cerium | IV, $(Ce_2)^{VI}$ | 140.25 |
| Th | * | Thorium | IV | 232.4 |
| Zr | * | *Zirconium* | IV | 90.6 |
| Al | * | ALUMINUM | $(Al_2)^{VI}$ | 27.1 |
| Er | * | *Erbium* | $(Er_2)^{VI}$ | 167.7 |
| Y | * | *Yttrium* | III | 88.7 |
| Gl | * | *Glucinum* (Beryllium) | II | 9.1 |
| Mg | * | MAGNESIUM | II | 24.32 |
| Ca | * | CALCIUM | II, IV | 40.07 |
| Sr | * | STRONTIUM | II, IV | 87.63 |
| Ba | * | BARIUM | II, IV | 137.37 |
| Li | * | LITHIUM | I | 6.94 |
| Na | * | SODIUM (Natrium) | I | 23.00 |
| K | * | POTASSIUM (Kalium) | I | 39.10 |
| Rb | * | *Rubidium* | I | 85.45 |
| Cs | * | *Cæsium* | I | 132.81 |
| | | POSITIVE END | | |

†Jour. Am. Chem. Soc., xxxviii, p. 2220.

These eighty-three elements are classed under two great divisions; viz., **metallic** and **nonmetallic.**

**METALLIC ELEMENTS,** the metals, or as they are frequently termed, the positive elements (denoted in the table by the*), usually having the ending "**um**" or "**ium,**" which signifies possessing metallic properties, are about sixty-two in number, and the study of these constitutes—

**METALLURGY.—The science of economically extracting metals from their ores, and applying them to useful purposes.**

**AN ORE is a mineral containing one or more metals in a free or combined state.** The chief ores from which metals are obtained are sulphides, oxides, or carbonates. In some instances metals are obtained in paying quantities from such ores as chlorides, arsenides, sulphates, phosphates, or silicates. Gold and platinum are usually found in a free metallic state, then they are termed "native." Tin, silver, copper, and some other metals are occasionally found native.

**GANGUE.—The foreign material or impurity in which minerals are found embedded** is variously known as "gangue," "veinstone," or "matrix." This may consist of such carbonates as calc-spar, limestone; such silicates as feldspar, hornblende, and mica; such sulphates as heavy-spar; and such fluorides as fluor-spar. This is separated from the mineral by the miner in crushing, sorting, and washing operations known as "dressing," after which the ore is sent to the metallurgist. Practically all this is now done at one plant known as the furnace or mill.

**SLAG is the fused metallic dross separated from the metal bearing compounds** when the minerals of

iron, copper, silver, nickel, and cobalt are fused with arsenic, sulphur, or silica. Oxides unite with the silica and form a part of the slag.

**REGULUS.—When the minerals of iron, copper and silver are smelted or fused with substances containing sulphur,** the resulting sulphide is known as "regulus" or "matte."

**SPEISS.—When the minerals of nickel and cobalt are similarly fused and converted into arsenides,** the combination is termed "speiss."

**REDUCTION is the process of freeing a metal from its combinations.** There are three methods employed, viz.: fusion, leaching, and gaseous. Any substance employed in effecting this result is called a "reducing agent." The chief reducing agents are carbon, hydrocarbons, carbon monoxide, and hydrogen. In this process metallic compounds are usually converted into oxides, if they do not already exist as such, which is generally accomplished by heating them in contact with atmospheric air. For example, when zinc carbonate is thus treated, the reaction or reduction is as follows:

$$ZnCO_3 \ (+\text{heat}) = ZnO + CO_2$$

Then by addition of the reagent carbon the metallic zinc is obtained thus:

$$2ZnO + C = 2Zn + CO_2$$

Sulphides are reduced by partially converting the metallic sulphide into an oxide, with the aid of heat, when the remaining metallic sulphide reacts with the oxide produced, freeing the metal, as for example:

$$PbS + 2PbO = SO_2 + 3Pb$$

These various processes are called "smelting."

**ROASTING: When metalliferous substances are reduced to oxides by heating, in contact with atmospheric air,** the process is called "**roasting.**" When they are similarly heated in contact with chlorine gas or with common salt, the operation is known as "**chlorinizing roasting.**"

**CALCINATION is the process of heating a substance at a temperature below its melting point.** The object is to expel all volatile and organic matter, and, in the case of an ore, to render it more porous preparatory to roasting or smelting.

**DISTILLATION.—The act of separating in the form of vapor the more volatile portions of a substance by heat,** and subsequently condensing them to a liquid state in some cooling receiver or worm. Mercury and zinc are extracted from their ores by this process, and the former metal is purified by redistillation.

**SUBLIMATION is an analogous process, except that the substance separated as a vapor is condensed as a solid.** For example, arsenic is sublimed from ores containing it.

**SCORIFICATION is the process of converting the foreign substance present in a metallic compound into slag by oxidation and union with silica.** The vessel in which the operation is effected is termed a "**scorifier.**"

**OCCLUSION is the property possessed by some metals of absorbing and retaining certain gases,** thus—iron absorbs carbonic oxide readily, silver occludes oxygen, platinum will absorb considerable quantities of oxygen and hydrogen, and it has been demonstrated that palladium foil under certain circumstances will absorb 982 volumes of hydrogen.

**CEMENTATION is the reaction which takes place under heat between two substances without fusion.**—Thus, when iron is heated with charcoal (carbon) a reaction takes place and the iron is said to become carburized. Such a reaction is known as "carburizing cementation." When iron is heated with red hematite, $Fe_2 O_3$, as an oxidizing agent, the impurities contained in it are modified or removed by the cement powder. Such a process is known as an "oxidizing cementation."

**DRY PROCESS.—The operation of separating metals from metallic combinations or metalliferous matter by the agency of heat.**

**WET PROCESS.—The operation of separating metals from metallic combinations or metalliferous matter by suitable solvents,** such as the ordinary acids, etc., and then precipitating those metals desired with proper reagents or by an electrochemical process.

Of the sixty-two elementary metals mentioned, only *fourteen* are ordinarily employed in their true *metallic condition.* These are:

| | | |
|---|---|---|
| Iron | Aluminum | Gold |
| Copper | Nickel | Silver |
| Lead | Antimony | Mercury |
| Zinc | Magnesium | Platinum |
| Tin | Bismuth | |

About twelve are more or less useful in the preparation of medicines, in the arts for coloring pigments, and for alloying purposes. These are:

| | | |
|---|---|---|
| Potassium | Barium | Cobalt |
| Sodium | Manganesium | Cadmium |
| Calcium | Arsenicum | Titanium |
| Lithium | Chromium | Uranium |

The remaining thirty-six are more or less rare, and many of them are of little or no practical value in the metallic state. However, the steel industry has been revolutionized by the use of some of these rare metals, such as vanadium, molybdenum, and tantalum in making alloys, and the use of tungsten in incandescent lamps and radium in medicine is indicative of the benefits which may be derived from further researches in metallurgic procedure.

The metallurgist groups the metals into two classes, which are known as *noble* and *base:*

**NOBLE METALS are those whose compounds with oxygen are decomposable by heat alone, at a temperature not exceeding redness. These are:**

| | |
|---|---|
| Mercury | Rhodium |
| Silver | Ruthenium |
| Gold | Osmium |
| Platinum | Iridium |
| Palladium | |

**BASE METALS are those whose compounds with oxygen are not decomposable by heat alone, retaining oxygen at high temperatures.**

The base metals are further subdivided with reference to their affinity for oyxgen and other chemical properties.

The First Division contains five metals. They are very readily oxidized, and their oxides are all soluble in water, giving it a strongly alkaline reaction; so also are their phosphates and carbonates, with the exception of lithium phosphate, which is quite insoluble, and the carbonate, which is only sparingly soluble. They all energetically decompose water at ordinary tempera-

tures, liberating hydrogen, and forming hydroxides in solution. They are soft, of low specific gravity, and fusible at low temperatures. These are:

| | |
|---|---|
| *Potassium* | Rubidium |
| *Sodium* | Cæsium |
| *Lithium* | |

THE SECOND DIVISION contains six metals, all of which decompose water at ordinary temperatures with the exception of magnesium, combining with the oxygen. Their oxides of the common metals are more or less soluble in water, rendering it alkaline; but their neutral carbonates and phosphates are insoluble. These are:

| | |
|---|---|
| *Barium* | *Calcium* |
| *Strontium* | *Magnesium* |
| *Glucinum (Beryllium)* | *Radium* |

THE THIRD DIVISION contains twelve metals, of which but three are of much importance. Those which have been isolated do not decompose water at ordinary temperatures without the addition of a weak acid or a slight rise of temperature. Their oxides and carbonates are insoluble in water. These are:

| | |
|---|---|
| *Aluminum* | Erbium |
| *Chromium* | Cerium |
| *Titanium* | Lanthanum |
| Thorium | Didymium |
| Yttrium | Tantalum |
| Zirconium | Columbium |

THE FOURTH DIVISION contains nine metals, the chief of which decompose water at a red heat. These are:

| | |
|---|---|
| *Iron* | *Uranium* |
| *Nickel* | Vanadium |
| *Cobalt* | Thallium |
| *Manganesium* | Indium |
| *Zinc* | |

THE FIFTH DIVISION contains four metals, which do not decompose water at any temperature. These are:

| | |
|---|---|
| *Cadmium* | *Bismuth* |
| *Lead* | *Copper* |

THE SIXTH DIVISION contains six metals. All the higher oxides of these metals have acid properties. These are:

| | |
|---|---|
| *Tin* | Molybdenum |
| *Antimony* | Tungsten |
| *Arsenic* | Tellurium |

The nonmetallic elements may be divided according to their physical states at ordinary temperatures, thus:

**Gases**

| | | |
|---|---|---|
| Oxygen | Nitrogen | Fluorine |
| Hydrogen | Chlorine | |

**Liquid**

Bromine

**Solids**

| | | |
|---|---|---|
| Carbon | Sulphur | Phosphorus |
| Boron | Selenium | Iodine |
| Silicon | | |

## CHAPTER II

## PROPERTIES OF METALS

**A METAL is an elementary substance, solid at ordinary temperatures, with the single exception of mercury (a liquid solidifying at—39° C.), having a peculiar luster, called metallic "luster," insoluble in water, a conductor of heat and electricity, possessing the quality of uniting with oxygen to form a basic oxide, and having the property of replacing hydrogen in chemical reactions, as, for example:**

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

No line can be sharply drawn between metals and nonmetals; just as no line can be drawn between soluble and insoluble, poisonous and nonpoisonous, substances. The two elements, arsenicum and tellurium may well be considered the intermediate links between the two classes.

All metals, when exposed in an inert atmosphere to a sufficient temperature, assume the form of liquids and present the following characteristic properties: They are practically nontransparent and reflect light in a peculiar manner, producing what is called metallic luster. When melted in nonmetallic vessels, they take the shape of a convex meniscus. When exposed to greater temperatures, some sooner, others later, pass into vapors. What these vapors are like is not known in many cases, since, as a rule, they can be produced only at very high temperatures precluding the use of

transparent vessels. Silver vapor is blue, that of potassium green, and many others—mercury, for example—colorless. The liquid metals, when cooled down sufficiently, some at lower, others at higher temperatures, congeal into compact solids, endowed with relative nontransparency and the luster of their liquids.

**NONTRANSPARENCY.**—Metals as a rule are nontransparent, or opaque, yet some have proved to possess the property of transparency in a low degree at least. In the case of gold, through the leaf, or thin films produced chemically on glass plate, a light green color is transmitted. This is ascribed to the gold aggregating and allowing white light to pass through the interstices. Also very thin films of mercury are said to transmit light with a violet-blue color, and copper, it is claimed, is somewhat translucent; while silver in thin films .000083 of an inch thick is opaque in an atmosphere of hydrogen or coal-gas, but in the air transparency begins at 240° C. and is quite complete at 390° C.

**COLOR.**—Most metals range from the pure white of silver and tin to the bluish hue of lead. Bismuth is a light gray, with a delicate tinge of red. Copper is called the "red metal." Gold is a rich yellow; barium and strontium a straw color, while calcium exhibits a little deeper shade of that color.

**LUSTER.**—Polished metallic surfaces, like those of other solids, divide any incident ray into two parts, of which one is refracted, while the other is reflected, with this difference, however, that the former is completely absorbed, while the latter, in regard to polarization, is quite differently affected, which fact, in all

probability, accounts for the peculiar property of metallic luster.

**ODOR AND TASTE.**—Most metals are destitute of odor and taste. Peculiar odors are, however, evolved from some of them when heated; in fact, one of the means of determining arsenicum consists in the recognition of its characteristic smell of garlic when heated. Iron, copper, or zinc when heated also evolve peculiar odors. The taste which is perceived in some is no doubt due to their peculiar character, although in some cases it may depend upon voltaic action set up by the chemical agency of the saliva, the metal not being perfectly pure. If a piece of zinc be placed upon the tongue, and a piece of silver under it, and the edges joined, a metallic taste will be perceived dependent upon slow solution of the zinc under galvanic action. The odor, Dr. Essig says, "may be noticed in a marked degree when holding in the hand a mass of an alloy composed of gold, platinum, tin, and silver prepared for use as amalgam." The moisture of the hand, aided by its heightened temperature, seems to promote the galvanic action.

**CRYSTALLINE FORM.**—Most metals are capable of crystallization, and their crystals belong to the following systems: *Regular*—Silver, gold, palladium, mercury, copper, iron, lead; *quadratic*—tin, potassium; *rhombic*—antimony bismuth, tellurium, zinc, magnesium.

Perhaps all metals assume a crystalline structure on congealing, differing only in degree of visibility. Antimony, bismuth, and zinc exhibit a very distinct crystalline structure plainly visible in broken ingots. Tin is also crystalline, which fact is evinced by the "tin cry"

when a bar of the metal is bent, the crystal faces sliding over one another; but the bar is not easily broken, and exhibits an apparently noncrystalline fracture. Gold, silver, copper, aluminum, cadmium, iron, lead, cobalt, and nickel are practically amorphous, the crystals being so closely packed as to virtually produce a homogeneous mass.

**MALLEABILITY, DUCTILITY, AND TENACITY** are properties possessed by some metals by virtue of the cohesive power of their molecules, and are to that extent kindred.

**Malleability is that quality possessed by a metal which permits it to be hammered or rolled into thin sheets without breach of continuity.** Many metals possess this property relatively, it being the most wonderfully exemplified in gold. Leaves of this metal have been produced .000027 of an inch in thickness, each grain of which will cover an area of 75 square inches.

**DUCTILITY.—Ductility is that property possessed by some metals by virtue of which they may be drawn into wire.** The operation consists in forcibly drawing the metal through a series of holes, which gradually decrease in size, in a hard-steel draw-plate. Gold is also the most ductile of all metals, a single grain of it having been drawn into a wire 550 feet in length. This was accomplished by covering the gold wire with silver, which is also remarkably ductile, thus making a composite wire of greater thickness. After drawing this down to the greatest possible degree of tenuity, the silver was dissolved off by nitric acid, leaving a gold wire .0002 of an inch in diameter.

**TENACITY.—Tenacity is that property possessed by metals in consequence of which they resist rupture**

**when exposed to tension.** Their relative tenacity may be ascertained by preparing wires of exactly equal diameters and comparing the number of pounds weight each will sustain before rupture.

These properties are shown relatively for some of the more important metals in the following table:

| Malleability | Ductility | Tenacity |
|---|---|---|
| 1. Gold | 1. Gold | 1. Iron |
| 2. Silver | 2. Silver | 2. Copper |
| 3. Copper | 3. Platinum* | 3. Platinum |
| 4. Aluminum | 4. Aluminum | 4. Silver |
| 5. Tin | 5. Iron | 5. Gold |
| 6. Platinum | 6. Nickel | 6. Zinc |
| 7. Lead | 7. Copper | 7. Tin |
| 8. Zinc | 8. Palladium | 8. Lead |
| 9. Iron | 9. Cadmium | |
| 10. Nickel | 10. Zinc | |
| 11. Palladium | 11. Tin | |
| | 12. Lead | |

The two properties of malleability and ductility are closely related to each other, yet, as may be seen from the above table, they do not always parallel each other, for the reason that ductility in a higher degree than malleability is determined by the tenacity of the metal; for example, tin, though quite malleable, is very slightly ductile, and iron, while ninth in point of malleability, is fifth in ductility. In the operation of hammering out a metal which the quality of malleability permits, the granular particles are flattened and spread in all directions, while in those allowed by its ductility each granular particle is elongated into a fiber.

*Some authorities give platinum first rank in ductility; though the majority are in accord with the above order.

There are several conditions which materially modify the properties of malleability, ductility, and tenacity, the most important of which are—

**Purity.**—Gold is the most malleable of all metals, yet if the merest trace of lead, itself a soft and malleable metal, be contained in it, the gold becomes too brittle to be worked, and especially is this the case if the gold has any silver also with it, as most gold has. This destruction of malleability and tenacity is still more pronounced when antimony or similar metals are mixed with gold, even in minute quantities.*

**Temperature** also exercises a very great modifying influence over these properties; for example, a bar of zinc obtained by casting is exceedingly brittle, but when heated to 100° or 150° C. it may be rolled into thin sheets or drawn into wire. Such sheet or wire then remains malleable and ductile after cooling. The explanation of this remarkable fact is, that the loosely cohering crystals have become intertwisted and forced into absolute contact with each other, and this is supported by the fact that the rolled zinc has a somewhat higher specific gravity than the original ingot. If the temperature be carried to 205° C. it again becomes so brittle that it may be powdered in a mortar. Extreme care, therefore, must be exercised in the handling of hot zinc dies, for if by accident one be dropped upon a hard surface it is likely to be spoiled. Aluminum, magnesium, and some other metals, which at ordinary temperatures possess little or no ductility, may be drawn into wire when heated.

These qualities are greatly diminished in alloys by heating. Some forms of brass, for example, which are

*See chapter on Gold.

soft, tenacious, and ductile at ordinary temperatures, are made quite brittle by heating to dull redness. Again it is quite certain that 18-carat gold solder is brittle at red heat.

The tenacity of metals in general is greatly diminished by heating. The exceptions to this are in the cases of iron, steel, and gold.

The following table shows the results obtained by Wertheim* in his experiments on a number of the metals at temperatures from 15° to 20° C.

| Name | For Wire 1 Square Mm. Section, Weight (in Kilos) Causing | |
|---|---|---|
| | Permanent Elongation of $\frac{1}{20000}$ | Breakage |
| Iron, drawn | 32.00 | 61.00 |
| " annealed | Under 5.00 | 47.00 |
| Copper, drawn | 12.00 | 40.00 |
| " annealed | Under 3.00 | 30.00 |
| Platinum, drawn | ..... | 34.00 |
| " annealed | ..... | 23.00 |
| Silver, drawn | 11.30 | 29.00 |
| " annealed | 2.60 | 16.00 |
| Gold, drawn | 13.50 | 27.00 |
| " annealed | 3.00 | 10.00 |
| Zinc, drawn | .75 | 13.00 |
| " annealed | 1.00 | .... |
| Tin, drawn | .45 | 2.45 |
| " annealed | .20 | .... |
| Lead, drawn | .25 | 2.10 |
| " annealed | .20 | 1.80 |

**Annealing.**—Pure iron, copper, silver, and other metals are easily drawn into wire, rolled into sheets, or flattened under the hammer. But all these operations render the metals harder, and detract from their plasticity. Their original softness can be restored to them by annealing, i. e., by heating them more or less and then plunging them into cool water, oil, etc. In the

*Annales de Chimie et de Physique (III.), xii.

case of iron, however, this applies only if the metal is perfectly pure. If it contains a few parts carbon per thousand, the annealing process, instead of softening the metal, gives it a "temper," meaning a higher degree of hardness and elasticity.*

**Welding.**—The process of joining two clean surfaces of a metal together by pressure is called welding. This property is possessed by iron at white heat, but lead and gold will cohere at ordinary temperatures in proportion to their purity. Two pieces of iron may be welded by a current of electricity sent through the junction, when the metal is heated by the resistance offered to the passage of the current.

**Thermite Welding.**—Based upon the discovery that finely divided oxides mixed in volumetric proportions with finely divided aluminum will, when ignited in one spot, produce a temperature of about 3000° C. within one-half minute, without any supply of heat or energy from the outside. The affinity of aluminum for oxygen is such that it draws the latter out of the metallic oxide, and combines with it, thus setting the metal free. For welding purposes, $Fe_2O_3$ is used.

**Forging.**—The process of hammering metals out into various shapes. Some metals may be forged while cold, while others must be hot. This process demonstrates a property of metals known as "solid flow."

**ELASTICITY.**—All metals are elastic to this extent, that a change in form brought about by stresses not exceeding certain limit values, will disappear when the stress is removed. Strains exceeding the "limit of elasticity" result in permanent deformation, or, if suf-

*See chapter on Iron.

ficiently great, in rupture. This property may be increased in some metals by compounding and alloying. Thus, iron compounded with the proper amount of carbon, has its elasticity increased to the very highest degree, while the metal itself is almost devoid of the quality. The same is true of copper and zinc, in some forms of brass, also of gold and platinum, when alloyed with copper; both are soft and possessed of little elasticity, yet when combined in proper proportions with copper, an alloy is produced which is quite elastic and may be used for clasps for artificial dentures.

**SONOROUSNESS.**—This is a property possessed by the harder metals, and is quite marked in certain alloys, such as those of copper and tin, known as bell-metal, and in steel wires which produce the sound in pianos. Lead, which is but feebly, if at all, sonorous, may become so, it is claimed, if cast in the shape of a mushroom. Aluminum emits a characteristic sound when struck. The first article known to have been made of aluminum was a baby rattle for the infant prince imperial of France, for which purpose it was well fitted on account of its sonorousness. Impurities sometimes increase the sonorousness of a metal, as in the case of antimony in lead.

**FUSIBILITY AND VOLATILITY.**—All may be fused, and most of them are capable of being volatilized, but the temperature at which they become fluid differs greatly in different metals, as the following table shows: greatly in different metals. It will be remembered that mercury is in a fused state and volatilizes to a limited extent at ordinary temperatures. Osmium readily volatilizes before fusion.

## PROPERTIES OF METALS*

| Name of Metal | Fusing Point, C. | Boiling Point, C. | Crystalline Form |
|---|---|---|---|
| Aluminum ..... | 657. | x2200. | octahedral |
| Antimony ..... | 630. | 1500-1700. | hexag. rhomb. |
| Bismuth ..... | 269. | 1435. | rhomb. |
| Cadmium ..... | 321.7 | 778. | crystalline |
| Cobalt ..... | 1464. | | |
| Copper ..... | 1084.-P | 2100. | crystalline |
| Gold ..... | 1060. | 2530. | regular |
| Iridium, sp. g. 15.86 | 2250. | | white spongy |
| " sp. g. 22.42 | 1950. | | reg. or hexag. |
| Iron, pure..... | 1505. | | cub. or reg. |
| " wrought .... | 1600. | | octahedral |
| " white pig... | 1075. | | |
| " gray " ... | 1275. | | |
| " steel ..... | 1375. | | |
| Lead ..... | 327. | 1580. | reg. or monocl. |
| Magnesium ..... | 632.6 | x2200. | |
| Manganese ..... | 1207. | | monoclinic |
| Mercury ..... | —38.85 | 357.33 | octahedral |
| Nickel ..... | 1435. | | |
| Osmium ..... | 2500. | | amorphous |
| Palladium ..... | 1546. | | reg. hexag. |
| Platinum ..... | 1753. | | |
| Potassium ..... | 62.5 | 757.5 | |
| Silver ..... | 961.5 $P_2$ | 2050. | |
| Sodium ..... | 97.6 | 877.5 | |
| Tin ..... | 170-232. $P_3$ | x2200. | |
| Zinc ..... | 419. | 918. | |

x greater than; P melts at 1065 in air; $P_2$ melts at 955 in air; $P_3$ varies with specific gravity.

## POUILLET'S SCALE OF TEMPERATURE†

| | |
|---|---|
| Incipient redness ..... | 525° C. |
| Dull red ..... | 700 |
| Cherry red ..... | 900 |
| Deep orange ..... | 1100 |
| White ..... | 1300 |
| Dazzling white ..... | 1500 |

*Van Nostrand's Chem. Ann., 1909.
†Sexton.

Metals may be characterized as *fixed* and *volatile*. Of their volatility we have little precise knowledge. The boiling points of a few are given in the following table:

| Name of Metal | Boiling Point | Authority |
|---|---|---|
| Mercury | 357.3° C. | Olsen |
| Cadmium | 778. ° C. | " |
| Zinc | 918. ° C. | " |
| Potassium | 757.5° C. | " |
| Sodium | 877.5° C. | " |

For practical purposes the volatility of metals may be classed as follows:

1. *Distillable below redness: Mercury.*
2. *Those distillable at red heats:*

| | |
|---|---|
| Cadmium | Potassium |
| Zinc | Sodium |
| Magnesium | |

3. *Those which are volatilized more or less readily when heated beyond their fusing points in open crucibles:*

| | |
|---|---|
| Antimony (very readily) | Tin |
| Lead | Silver |
| Bismuth | |

4. *Those which are with very great difficulty volatilized, if at all:*

| | |
|---|---|
| Gold | Copper (?) |

5. *Those which are practically fixed, or nonvolatile:*

| | |
|---|---|
| Copper (?) | Aluminum |
| Iron | Lithium |
| Nickel | Strontium |
| Cobalt | Barium |
| Calcium | |

"In the oxyhydrogen flame silver boils, forming a blue vapor, while platinum volatilizes slowly, and osmium, though infusible, very readily."*

"It is doubtful," says Makins, "if gold is volatile *per se*. But if gold be alloyed with copper, it has been shown by Napier to be considerably volatilized, so that quantities, amounting to 4½ grains, could be collected during the pouring out of 30 pounds weight from a crucible. * * * That mixtures of gold, silver, and lead, when cupellated together, volatilize considerably."

**SPECIFIC HEAT.**—Equal weights of different metals have been found to absorb different amounts of heat when subjected to the same temperature. They, indeed, possess different capacities for heat. Thus, the amount of heat necessary to raise a given weight of water has been found to be 31 times as great as that required to raise an equal weight of platinum through the same interval of temperature; or, in other words, the amount of heat required to raise a given weight of water through 100° C. will raise 31 times the same weight of platinum through 100° C. of temperature. Thus, water being taken as the standard or unit, the specific heat of platinum is $\frac{1}{31}$ or 0.032 that of water.

TABLE OF SPECIFIC HEATS AT 0° C.

| | |
|---|---|
| 1. Iron | 0.1162 |
| 2. Nickel | 0.1084 |
| 3. Cobalt | 0.1030 |
| 4. Zinc | 0.0935 |
| 5. Copper | 0.0936 |
| 6. Palladium | 0.0592 |
| 7. Silver | 0.0559 |
| 8. Cadmium | 0.0548 |

*William Dittmar.

9. Tin ..... 0.0545
10. Antimony ..... 0.0495
11. Mercury ..... 0.0334
12. Gold ..... 0.0316
13. Platinum ..... 0.0323
14. Lead ..... 0.0310
15. Bismuth ..... 0.0301
16. Aluminum ..... 0.2220

**EXPERIMENT No. 1.**—Prepare bullets of exactly equal weights of several of the above metals, such as zinc, silver, cadmium, tin, and lead; expose them to the same temperature, for the same length of time, and then drop them simultaneously upon a sheet of wax placed across an open side of a pasteboard box. They will be observed to melt their way through or into the wax in the order named.

**EXPANSIBILITY.**—The expansion of metals by heat varies greatly. The coefficient of expansion is constant only in metals that crystallize in the *regular system.* The others expand differently in the direction of the different axes, and to eliminate this source of uncertainty in making estimates of their expansibility, these metals are employed as compressed powders.

| Name of Metal | Expansion 0° to 100° C |
|---|---|
| Platinum, cast | 0.000907 |
| Gold, cast | 0.001451 |
| Silver, cast | 0.001936 |
| Copper, native | 0.001708 |
| Copper, artificial | 0.001869 |
| Iron, soft | 0.001228 |
| Steel, cast | 0.001110 |
| Bismuth, mean expansion | 0.001374 |
| Tin, compressed powder | 0.002269 |
| Lead, cast | 0.002948 |
| Zinc | 0.002905 |
| Cadmium, compressed powder | 0.003102 |
| Aluminum, cast | 0.002336 |
| Mercury | 0.018153 |

The preceding table gives the linear expansion from 0° to 100° C., according to Fizeau, the length at 0° being taken as unity:*

"The high rate of expansibility of zinc renders it particularly valuable as a metal for dies upon which to form plates for the mouth in many cases. The metal is cast while fluid and at its extreme limit of expansion, which upon cooling returns to its minimum dimensions, and thus furnishes a cast a little smaller than the plaster model which it represents. It has been found that this contraction of the zinc die a trifle more than compensates for the expansion which takes place in the plaster model in setting, and in the majority of cases a plate made thereon adapts itself more accurately to the mouth than one made upon a die of less expansible metal. Even if the contraction undergone by the zinc is so great as to produce a die somewhat smaller than the mouth, so far from being a detriment, it is a positive advantage in most cases of full upper replacement, as under such conditions the pressure of the finished plate is greater upon the alveolar ridge than upon the central portions of the hard palate—a state of affairs the advantages of which are sufficiently obvious without explanation."*†

**CONDUCTIVITY.**—Metals are good conductors of heat and electricity, but these qualities are very differently exhibited in different metals. All conductors tend to obey Ohm's law; viz., the current is directly proportional to the electro motive force and inversely proportional to the resistance. Metals are generally believed to convey electric current around the con-

*William Dittmar.

†Dr. E. C. Kirk, Am. System of Dentistry, iii, p. 793.

ductor and heat within the conductor, but neither have been definitely proved. The ratio of heat and electricity in good conductors is very nearly constant and is proportional to absolute temperature.

The following table gives the thermic and electric conductivities of some of the more important metals and alloys:

| Name of Metal | Electrical conductivity at 0° C. | Thermal conductivity at 0° C. Ag 1.00 |
|---|---|---|
| Silver | 681200 | 1.000 |
| Copper | 640600 | .7198 |
| Gold | 468000 | .7003 |
| Aluminum | 324000 | .3435 |
| Zinc | 186000 | .2653 |
| Cadmium | 146000 | .2213 |
| Nickel | 144200 | .1420 |
| Iron | 131000 | .1665 |
| Platinum | 91200 | .1664 |
| Tin | 76600 | .1528 |
| Lead | 50400 | .0836 |
| Antimony | 27100 | .0442 |
| Mercury | 10630 | .0148 |
| Bismuth | 9260 | .0177 |

Makins states that among the results of Dr. Matthiessen's experiments upon the electric conductivity of metals "are the facts that impurity of a metal or alloying it greatly diminishes its conducting power. Rise of temperature again has the same effect. Thus between 0° C. and 100° C. great diminution takes place, and that not uniformly, as some lose it much more in proportion than others, by thus raising the temperature. Many lose as much as twenty-five per cent of their conducting power."

An illustration of the comparative conductivity of the metals is illustrated in the electric furnaces with platinum coils. The electricity is readily transmitted

| Name of Metal | Specific Gravity | Authority |
|---|---|---|
| Lithium | 0.534 | John C. Olsen, A.M., Ph.D. |
| Potassium | 0.862 | " " |
| Sodium | 0.9735 | " " |
| Rubidium | 1.52 | " " |
| Calcium | 1.415 | " " |
| Magnesium | 1.69-1.743 | " " |
| Cæsium | 1.87 | " " |
| Glucinum | 1.85 | " " |
| Strontium | 2.54 | " " |
| Aluminum | 2.583 | " " |
| Barium | 3.75 | " " |
| Zirconium | 4.15 | " " |
| Vanadium | 6.025 | " " |
| Gallium | 5.95 | " " |
| Lanthanum | 6.154 | Lecoq de Boisbaudran |
| Didymium | 6.544 | Hillebrandt and Norton |
| Cerium | 7.042 | Hillebrandt and Norton |
| Antimony | 6.62 | Marchand and Scheerer |
| Chromium | 6.92 | Wöhler |
| Zinc | 7.142 | Karsten |
| Manganesium | 7.42 | Brunner |
| Tin | 7.294 | |
| Indium | 7.12 | Richter |
| Iron | 7.844 | Berzelius |
| Nickel | 8.6-8.93 | Richter |
| Cadmium | 8.642 | Schroder |
| Cobalt | 8.71 | |
| Molybdenum | 8.6-9.01 | Debray |
| Copper | 8.91 | |
| Bismuth | 9.747 | Holzmann |
| Silver | 10.53 | Holzmann |
| Lead | 11.34 | Deville |
| Palladium | 11.4 | Deville and Debray |
| Thallium | 11.85 | Crookes |
| Rhodium | 12.1 | Bunsen |
| Ruthenium | 8.6 | Deville and Debray |
| Mercury | 13.595 | H. Kopp |
| Tungsten | 18.77 | Wöhler |
| Uranium | 18.68 | Péligot |
| Gold | 19.32 | Matthiessen |
| Platinum | 21.48 | |
| Iridium | 15.86 | |
| Osmium | 22.477 | Deville and Debray |

from its source by the copper efferent wire, but when it meets the platinum that metal offers so much resistance to the passage of the current, on account of its low conducting power, that it becomes white-heated—incandescent.

**SPECIFIC GRAVITY.**—This property varies in different metals from 0.534 (lithium) to 22.477 (osmium), as shown in the table on page 42.

## CHAPTER III

## COMPOUNDS OF METALS AND NONMETALS

Metals unite with each other *indefinitely* to form alloys, preserving the metallic appearance and properties. They combine with nonmetals in *definite* chemical proportions to form compounds of a more precise nature, in which case the metallic characters are almost invariably lost. These definite compounds include the

| | |
|---|---|
| Oxides | Fluorides |
| Sulphides | Cyanides |
| Chlorides | Selenides |
| Bromides | Tellurides |

They also combine with

| | |
|---|---|
| Nitrogen | Silicon |
| Phosphorus | Carbon |
| Boron | |

forming nitrates, phosphates, and phosphides, borates, etc.

**METALLIC OXIDES.—All metals combine with oxygen to form oxides,** and most of them in several proportions. As a class they exhibit a greater disposition to unite directly with oxygen than the nonmetals, though few of them will do so in their ordinary condition and at ordinary temperatures. Several metals, such as iron and lead, are superficially oxidized when exposed to the air under ordinary conditions, but this would not be the case unless the air contained water and carbon dioxide, which greatly favor oxidation.

Among the more important metals, five only are oxidized in dry air at ordinary temperatures, viz., potassium, sodium, barium, strontium, and calcium. The affinity of these metals for oxygen is so great that they must be kept under naphtha ($C_{10}H_{16}$) or some substance containing no oxygen.

**EXPERIMENT No. 2.**—With a knife cut off a small piece of metallic sodium; observe it exhibits a brilliant luster but speedily tarnishes by combining with the oxygen of the air, forming the oxide (NaO) of sodium. Plunge the sodium into a jar of oxygen; it takes fire and burns with a brilliant yellow flame.

Zinc on the other hand exhibits no disposition to combine with oxygen at ordinary temperatures, but is induced to do so at a moderate heat (1040° C.), when it burns with a beautiful greenish flame, produced by the union of its vapor with the oxygen of the air, forming zinc oxide—ZnO.

**EXPERIMENT No. 3.**—With a piece of zinc foil form a tassel, gently warm the end, dip into a little flowers of sulphur, kindle, and let down into a jar of oxygen, when the flame of the burning sulphur will ignite the zinc, which burns with great brilliancy, forming oxide of zinc.

A large number of the metals are oxidized during fusion. Lead, for example, may be entirely transformed into its oxide by continued exposure to sufficient heat. The oxides of others may be formed by heating a carbonate or nitrate of the metal to redness. For example, if $ZnCO_3$ be heated to a red heat $CO_2$ is evolved, leaving the pure zinc oxide (ZnO). Again the oxide of copper may be obtained by digesting that metal in nitric acid,—$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$—forming the nitrate of copper, which then

may be decomposed by heat into nitric and cupric oxides.

They are also formed from some salts; for example, if to a solution of sulphate or chloride of iron ammonium hydrate be added the hydrated sesquioxide of iron ($Fe_2(OH)_6$), the antidote for arsenic is formed. And zinc oxide may be obtained by adding potassium hydroxide to a solution of zinc sulphate.

Deflagrating some metals with an oxidizing agent produces an oxide of the metal. Advantage is taken of this in rendering brittle gold malleable by roasting it with nitrate of potassium.* The contaminating tin, lead, zinc, antimony, etc., combine with the oxygen of the nitrate to form oxides, and are dissolved in the molten flux.

Other metals, such as gold, platinum, iridium, rhodium, and ruthenium, do not combine directly with oxygen, their combination being effected only by indirect means, and with difficulty.

**Oxidizing Agents** are substances such as—

| | |
|---|---|
| Oxygen (O), | Potassium chlorate ($KClO_3$) |
| Air (O and N), | Sodium chlorate ($NaClO_3$), |
| Water ($H_2O$), | Iron tetroxide ($Fe_3O_4$), |
| Potassium nitrate ($KNO_3$) | Iron trioxide ($Fe_2O_3$), |
| Sodium nitrate ($NaNO_3$) | Carbon dioxide ($CO_2$) |

which, imparting a part or the whole of their oxygen to another substance, cause it to become oxidized; conversely—

**Deoxidizing Agents** are substances such as—

| | |
|---|---|
| Carbon (C), | Compounds of hydrogen |
| Carbon Monoxide (CO), | and carbon—hydrocarbons |
| Hydrogen (H), | and sometimes metals, |

*See chapter on Gold.

which reduce oxides by combining with the oxygen which they may contain.

Examples of oxidation—

$$Zn + O = ZnO$$
$$3FeCO_3 + O = Fe_3O_4 + 3CO_2$$
$$3FeO + CO_2 = Fe_3O_4 + CO$$

Examples of deoxidation—

$$2KClO_3 + C_3 = 2KCl + 3CO_2$$
$$Fe_2O_3 + H_6 = Fe_2 + 3H_2O$$
$$Fe_2O_3 + 3CO = Fe_2 + 3CO_2$$

**Substitution or Replacement.**—Just as chlorides are derived by substitution from hydrochloric acid, HCl, so may oxides be represented as being derived from one or more molecules of water, $H_2O$, by the substitution of a metal for hydrogen; with this difference, however, that water contains two atoms of hydrogen; therefore, the replacement may be only partial, producing the hydrated oxide, or complete, forming the oxide. Thus the monoxides may be formed by the replacement of both atoms of hydrogen by a monad, as $Na_2O$, $Ag_2O$, or a dyad, CuO, ZnO; while the higher oxides may be regarded as two or more molecules of water, in which the hydrogen in a similar manner is replaced by its equivalent of metal, as $MnO_2$, $Al_2O_3$.

The oxides may be classed as **Basic Oxides** and **Acid-forming Oxides.**

**Basic Oxides.**—When the replacement of the hydrogen is complete, the resulting compound is a basic oxide—$K_2 + H_2O = K_2O + H_2$.

**Hydroxides.**—When the replacement of the hydrogen is incomplete, the resulting compound is a hydroxide—$K + H_2O = KHO + H$, or with the dyad calcium, $Ca + 2H_2O = Ca2HO + H_2$.

Bases neutralize acids either partially or entirely, replacing either a part or all of their hydrogen. thus we have $KHSO_4$ and $K_2SO_4$, which are salts.

**An alkali** is only a class of base, and might be defined as a base which is very soluble in water, as $K_2O$ and $Na_2O$.

It will be observed that metals are capable of forming bases by combining with oxygen, or salts by combining with salt-radicals. Many metals,* however, form acid-forming oxides or anhydrides; thus tin forms stannic anhydride ($SnO_2$), and antimony forms antimonic anhydride ($Sb_2O_5$), and it is always found that the acid-forming oxide of a metal contains a larger proportion of oxygen than any of the other oxides which the metal may happen to form, thus:

**The Acid-forming Oxides** are those metallic oxides, or anhydrides which form acids with water, as in the case of nonmetallic oxides.

A number of metallic oxides are found in nature as ores from which the metals are reduced. Tin occurs as tinstone, $SnO_2$, iron as $Fe_2O_3$, and $Fe_3O_4$, etc.

**REDUCTION OF METALLIC OXIDES.**—The variable affinities exhibited by the metals for oxygen groups them into two classes already known as noble and base metals.

**Reduction of the Oxides of the Noble Metals.**—So feeble is the affinity of the noble metals for oxygen

*See Sixth Division, Chapter I.

that their oxides are easily decomposed and the metals reduced without the aid of any other agency than that of simply heating to redness—about 700° C.

**Reduction of the Oxides of the Base Metals.**—On the other hand the base metals exhibit a very strong affinity for oxygen and the mere application of heat will not reduce them. Indeed, in many instances a decided increase of temperature serves only to strengthen their affinity and hence increases the proportion of oxygen in the compounds previously formed. Therefore, in addition to heat the assistance of some substance is required whose affinity for oxygen is stronger than that of the metal and will, when favored by heat, abstract the oxygen from the oxide. Thus, the oxide of lead may be formed by heating the carbonate:

$$PbCO_3(+\text{heat}) = PbO + CO_2,$$

and driving off the carbon dioxide ($CO_2$). The lead oxide (PbO), however, can not be further reduced to metallic lead by heat; on the contrary, if the heating be continued, the production of a higher oxide only will be effected. But if, in addition to heating, the oxidized lead be covered with a layer of pulverized charcoal, which will abstract the oxygen for its own use, uniting with it to form carbon dioxide, the lead will be reduced or liberated. Such a reduction is accomplished by the reducing or deoxidizing agent, carbon, the action being *favored by heat:*

$$2PbO + C\ (+\text{heat}) = 2Pb + CO_2.$$

When the lead and zinc used for counter-dies and dies in the laboratory are overheated or subjected to frequent or long continued meltings, they become par-

tially oxidized and covered with an earthy looking mass consisting of partially oxidized metal. A continued exposure to heat would, as we have observed, have the effect of converting this into an oxide of a higher degree, but if the molten metal be covered with pulverized charcoal or carbonaceous substance, such as oil, fat, suet, or scraps of beeswax (hydrocarbons), the oxygen of the oxide will be abstracted, carbon dioxide

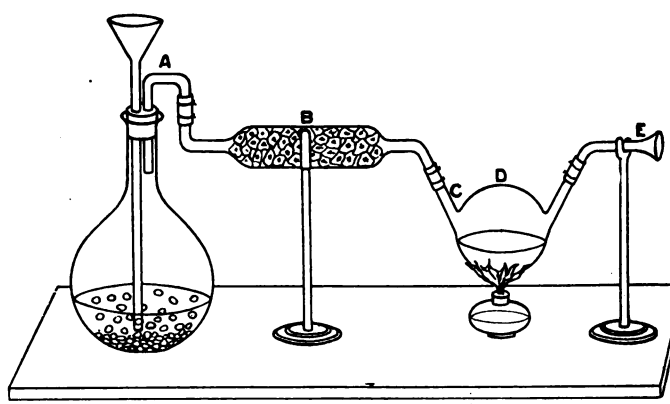


Fig. 1.

formed and evolved, while the metal will be reduced to a free state.

**Reduction with Hydrogen.**—Other oxides which can not be reduced by deoxidizing agents favored by the conditions as stated above may, by the assistance of proper apparatus and heat, be reduced by a current of dry hydrogen.

**EXPERIMENT No. 4.**—Pass the delivery tube of an ordinary hydrogen generator (A, Fig. 1) into one end of a drying tube (B), well filled with fragments of calcium chloride, for the pur-

pose of absorbing the moisture which may be carried over with the gas; connect the other end of the drying tube with a tube (C) upon which a bulb (D) has been blown for the reception of the metallic oxide. After the gas has completely driven the air out of the apparatus, heat is applied to the bulb containing the oxide. As the dry hydrogen flows over the heated oxide in a strong stream it combines with the oxygen—favored by heat—and passes out of the tube (E) as aqueous vapor, while the metal is left free.

**Reduction with Sulphur.**—Some oxides may be best reduced by heating with sulphur, in which case sulphur exhibits a greater affinity for the oxygen than the metal does, and abstracting it, forms sulphur dioxide ($SO_2$). A portion of the sulphur, however, combines with the metal, converting it into a sulphide or sulphate, or a mixture of both. The reduction of such compounds is treated under metallic combinations with sulphur.

**Reduction with Chlorine.**—There are a few oxides which may be reduced by chlorine gas. Thus platinum oxide is reduced in a current of dry chlorine.

**EXPERIMENT No. 5.**—Repeat Experiment No. 4, using calcium oxide in the drying tube, and dry chlorine gas.

**METALLIC SULPHIDES.**—Metals combine directly with sulphur to form a class of compounds which, from a chemical and economical point of view, are almost as important as the oxides, since the ores of many of the most important metals are found as sulphides, as for example, galena (PbS); stibnite ($Sb_2S_3$); zinc-blende (ZnS); greenockite (CdS); copper-glance (CuS); iron pyrites ($FeS_2$); cinnabar (HgS); silver glance ($Ag_2S$), etc. These are generally brittle solids possessing so high a degree of luster that some of them have been mistaken for gold, hence iron pyrites has

been called "fool's gold." In composition they resemble the oxides and hydroxides, with many of which they are analogous. The exceptions to this analogy are the alkalies and alkaline earths, there being but two oxides of potassium, sodium, and barium, while there are no less than five sulphides of these metals. All the metallic sulphides are solid at ordinary temperatures; most of them fuse at red heat, and some sublime unchanged. When roasted in air at high temperatures, they are converted into sulphates; ($ZnS + O_4$ favored by high heat $= ZnSO_4$), or, if they are exposed to higher and continued heat, into oxides.

They may be prepared by heating the metals or their oxides with sulphur, from the sulphates by heating them with charcoal, deoxidizing them, and from their soluble salt solutions by adding sulphuretted hydrogen.

**EXPERIMENT No. 10.**—To the following salt solutions in several test tubes add a few drops of sulphuretted hydrogen:

| | | | |
|---|---|---|---|
| $Pb(C_2H_3O_2)_2$ + Lead acetate | $H_2S =$ | $PbS$ + Lead sulphide (Black) | $2HC_2H_3O_2$ |
| $2AsCl_3$ + Arsenious Chloride | $3H_2S =$ | $As_2S_3$ + Arsenious Sulphide (Lemon Yellow) | $6HCl$ |
| $Cd(NO_3)_2$ + Cadmium Nitrate | $H_2S =$ | $CdS$ + Cadmium Sulphide (Yellow) | $2HNO_3$ |
| $2SbCl_5$ + Antimonic Chloride | $5H_2S =$ | $Sb_2S_5$ + Antimonic Sulphide (Orange Yellow) | $10HCl$ |

$Zn(C_2H_3O_2)_2 + H_2S = ZnS + 2HC_2H_3O_2$
Zinc acetate — Zinc sulphide (White)

$HgCl_2 + H_2S = HgS + 2HCl$
Mercuric chloride — Mercuric sulphide (1st White) (2d Yellow Orange) (3d Brown) (4th Black)

**REDUCTION OF THE METALLIC SULPHIDES.**—Since the ores of many of the most important metals are sulphides, and it is from such compounds that we derive our chief supply of copper, lead, mercury, silver, antimony, and several other metals, the subject of their reduction is of great importance.

**Flotation Process.**—Within the last decade metallurgists have devised such ingenious methods of recovering metals from their ores on a higher percentage basis that many of the old ore dumps and slime beds are being worked over at a profit. The flotation process which is merely a preparatory stage in reduction has developed since 1912 to the stage of handling 20,000,000 tons of ore annually. It is essentially a slimes process, that is the ore bearing mineral is reduced to a very fine powder by passing through jaw and gyratory crushers, rolling and ball mills, and various screens until finally it is reduced to a fine powder. To this is added an oil, usually a pine oil or creasol or creasote compound. This mixture or slime of sulphides, silicious or earthy gangue, oil and water is brought gently onto the surface of still water in a direction forming an acute angle with the surface of the water. The gangue, which has a greater adhesive

preference for the water than the oil, sinks while the sulphides have a greater adhesive preference for the oil and the larger portion of it floats. This is known as film flotation. If to these slimes a small quantity of acid, or alkali, or oil with an acid or alkali, is added and gas bubbles are introduced from below the sulphide, particles are brought to the surface and collect as a froth. This is known as froth flotation. These bubbles survive long enough to perform the metallurgic duty of carrying these particles of rich ore to the surface where they are collected and dewatered by various filtering, decanting, and evaporating processes until the cake has reached a minimum content of moisture of about 14 per cent, when it is ready for further dehydrating treatment preparatory to roasting. The various physical phenomena involved are surface tension, adsorption, adhesion and viscosity though colloidal conditions and electrostatic forces may play an important part, the latter being suggested by the fact that the sulphides most amenable to flotation are good conductors of electricity. Originally about three tons of oil were added to one ton of ore. Now from 0.5 to 0.75 of a pound of oil is added to each ton of ore with greater success in handling. Copper, lead, and zinc are now obtained in large quantities by means of this process and where these ores carry any precious metals as in argentiferous galena their recovery adds to the total values.

**Reduction by Heat.**—The reduction of some of the metallic sulphides, such as gold, platinum, silver, and mercury, is effected by heat alone. The oxygen of the air unites with the sulphur, which is evolved as sulphur dioxide, $SO_2$. In some instances, however, a por-

tion of the oxygen combines with the metal, and an oxide instead of the free metal is obtained. In some cases the sulphide is oxidized and converted into a sulphate, which in turn may be decomposed at high temperatures, separating into sulphur dioxide and free metal, or, at times, a metallic oxide. Then, again, some of the sulphides may, when roasted in air, be converted into permanent sulphates capable of resisting high degrees of heat.

**Reduction with Iron.**—Iron exhibits a strong affinity for sulphur and when favored by heat will abstract it from several metals, such as silver, lead, etc. Thus, if the sulphide of lead (galena) be heated with scraps of iron, metallic lead is freed:

$$PbS + Fe = FeS + Pb$$

or in the case of silver

$$Ag_2S + Fe = FeS + 2Ag.$$

**Reduction with Hydrogen.**—The sulphides of such metals as antimony, bismuth, copper, tin, and silver are decomposed by passing a current of dry hydrogen over them at a red heat, the metal being reduced, while the hydrogen combines with the sulphur, forming sulphuretted hydrogen:

$$CuS + 2H = H_2S + Cu.$$

**Reduction with Chlorine.**—Dry chlorine gas also decomposes some metallic sulphides, combining with both metal and sulphur.*

**Reduction with Acids.**—Nitrohydrochloric acid con-

*Three chlorides of sulphur are known, even though both elements are negative. They are $Cl_2S_2$, $Cl_2S$, and $Cl_4S$, the last in combination as $SnCl_4(Cl_4S)_2$.

verts the sulphides into chlorides, and hydrochloric acid in a few instances, acts similarly; its hydrogen combining with the sulphur is evolved as sulphuretted hydrogen. Strong nitric acid also decomposes them, the sulphur being oxidized and the liberated metal combines with the acid to form a nitrate. Mercuric sulphide is the only one that can not be thus reduced.

**METALLIC CHLORIDES.**—All metals combine with chlorine, and some of them in several proportions; thus we have stannous ($SnCl_2$) and stannic chlorides ($SnCl_4$).

Some of the chlorides occur in nature, those of silver (AgCl) and mercury ($Hg_2Cl_2$) as minerals, and those of sodium and potassium in enormous quantities in the solid state and dissolved in waters.

They may be regarded as derived, like the oxides, from a type—HCl—substituting for the hydrogen of one or more molecules of hydrochloric acid an equivalent in metal, thus:

From 1HCl, are derived monochlorides like KCl.
" 2HCl " " dichlorides, " $SnCl_2$.
" 3HCl " " trichlorides, " $AuCl_3$.
" 4HCl " " tetrachlorides, " $SnCl_4$.

**Preparation.**—They may be prepared by the action of hydrochloric acid upon the metals. Zinc, tin, cadmium, iron, nickel, and cobalt may be readily dissolved by hydrochloric acid, forming chlorides respectively and liberating hydrogen:

$$Zn + 2HCl = ZnCl_2 + H_2$$

They are also prepared by the action of nascent chlorine developed by the mixture of nitric with an excess

of hydrochloric acid. Gold and platinum are dissolved in this mixture (aqua regia) and stannic chloride is formed by its action on tin.

Some are also prepared by subjecting the metal or its oxide to a current of dry chlorine gas. In this manner the chlorides of titanium, aluminum, and chromium may be formed.

Sometimes a chloride is prepared by the substitution of one metal for another, thus stannous chloride may be made by distilling metallic tin with mercuric chloride:

$$HgCl_2 + Sn = SnCl_2 + Hg.$$

Other chlorides may be prepared by dissolving the oxides, hydroxides, or carbonates of the metals in hydrochloric acid.

**REDUCTION OF METALLIC CHLORIDES.**—The chlorides of gold and platinum may be decomposed by heat alone. Gold possesses so feeble an affinity for chlorine that solutions of the cloride of gold may be decomposed by mere exposure to light or atmospheric air. Solutions of sugar, gum arabic, oxalic acid, etc., readily decompose it.*

Silver chloride yields pure silver and emits an odor of hydrochloric acid when heated strongly on charcoal. When placed in water acidulated with hydrochloric or sulphuric acid, silver chloride may be reduced by stirring with small pieces of iron or zinc; the reaction is as follows:

$$Fe + H_2SO_4 = FeSO_4 + H_2, \text{ and}$$
$$2H + 2AgCl = 2HCl + 2Ag. \dagger$$

*See chapter on Gold.
†See chapter on Silver.

With the exception of the chlorides of the alkalies and alkaline earths all other chlorides may be decomposed by heating them in a current of hydrogen, hydrochloric acid and the pure metal being the result; but the evolution of the hydrogen must be well maintained, in order to drive off the hydrochloric acid formed, or it will react with the pure metal, forming fresh chloride.

Some chlorides may be decomposed by heating them with a metal which has a more powerful affinity for chlorine; thus, aluminum chloride may be reduced by heating it with sodium.

Sulphuric acid decomposes some chlorides and converts them into oxides, the oxygen being supplied by the water present.

**METALLIC BROMIDES.**—Bromine, though less active than chlorine, unites directly with most of the metals forming compounds analogous to the chlorides and resembling them closely in general properties.

Silver bromide (AgBr) analogous to the chloride is found as a natural mineral. Nearly all bromides are soluble, and those of the alkali metals are found abundantly in sea water and in many saline springs.

**REDUCTION OF METALLIC BROMIDES.**—The bromides are decomposed by oxidizing agents with liberation of bromine. The affinity of bromine for the metals being inferior to that of chlorine, the latter will, with the aid of heat, displace the bromine and form chlorides, but bromine can not be displaced in a like manner by iodine:

$$KBr + Cl = KCl + Br.$$

**METALLIC IODIDES.**—Many metals unite directly with iodine, forming compounds analogous to the chlorides and bromides. The iodides of potassium and sodium exist abundantly in sea water and in some springs, and the iodide of silver occurs as a natural mineral. Most of them are soluble in water, lead iodide being only slightly so, while the iodides of mercury and silver are quite insoluble.

A few of them, gold, silver, platinum, and palladium, are decomposed by heat alone, giving up their iodine. Ozone promptly decomposes all iodides, while atmospheric oxygen decomposes those of iron and calcium slowly. The superior affinity of chlorine and bromine enables these elements to displace iodine and form analogous chlorides or bromides:

$$KI + Cl = KCl + I, \text{ or}$$
$$KI + Br = KBr + I.$$

**METALLIC FLUORIDES** are formed by heating certain metals in the presence of hydrofluoric acid; by the action of that acid on metallic oxides; by heating electronegative metals, such as antimony, with the fluoride of lead or mercury. Volatile metallic fluorides may be prepared by heating fluor-spar with sulphuric acid and the oxide of the metal. With some metals fluorine occurs as a natural mineral, as with calcium ($CaF_2$), and the double fluoride of aluminum and sodium ($Al_2F_6, 6NaF$).

The fluorides are devoid of metallic luster; most of them are easily fusible and for the most part resemble chlorides.

**METALLIC CYANIDES** are formed by the union of metals with the compound radical cyanogen, CN.

Potassium and some other metals are converted into cyanides by heating them in cyanogen gas or the vapor of hydrocyanic acid.

Cyanides very closely resemble the chlorides, bromides, iodides, and fluorides.

**METALLIC SELENIDES.**—The element selenium very closely resembles sulphur in its chemical properties; hence, it combines with metals in much the same manner. Native selenides are rarely found.

**REDUCTION BY ELECTRICITY.**—Probably the most powerful means of reducing metals from their combinations with nonmetallic elements is obtained through the agency of electricity. To accomplish this, a solution of the metallic salt is subjected to the action of the galvanic current, and decomposed thereby.* This is simply and beautifully demonstrated by hanging a strip or coil of zinc in a solution of lead nitrate. After a few hours the zinc passes into solution, and exquisite crystals of lead have taken its place.

The electric furnace of Eugene H. and Alfred H. Cowles, of Cleveland, Ohio, has greatly advanced the production of such metals as aluminum from corundum, boron from boracic acid, and silicon from quartz. The furnace is constructed in the form of a rectangular box of fire-resisting material, lined with a mixture of fine charcoal and lime. It has a removable cover, which is perforated with openings to allow the escape of gases evolved. In the sides of this furnace the electrodes, two plates of gas carbon, are let in by means of which a powerful electric current is introduced. The charge

*The reduction of iron in the electric furnace is not carried on in this manner, as we ordinarily conceive of the term solution, though the ore is reduced after being liquefied by the intense heat produced by the carbon arc.

consists of the coarsely crushed ore and coke fragments. The essential feature of the process consists, therefore, in employing in the furnace a substance like carbon, whose high resistance to the passage of the current causes the production of a prodigiously high temperature, and which at the same time, is capable of exercising a powerful reducing action on the ore.

In very recent years the reduction of ores by electrolysis has given indications of superseding the older blast and reverberatory furnace methods. The principal reasons for this are (1) the production of electrical energy by water power, generally within the immediate vicinity, and without the aid of fuel, and (2) a purer quality of product. The purest and best grades of copper for electrical purposes are reduced from the ore by electrolysis, and Dr. Heroult, inventor of the "Heroult electric furnace," states that analyses prove that electrolytic steel shows 20 per cent higher tensile strength and elongation than ordinary steel.

## CHAPTER IV

## MELTING METALS

**REFRACTORY MATERIALS.**—Dentists frequently have occasion to use refractory materials, indeed they are using refractories of some sort in every day practice, but probably have never considered them as such. A refractory substance is one which is capable of withstanding high temperatures without marked changes in form or composition, and its value in the industrial world is in direct proportion to this, the predominating property.

In the natural state they are found as asbestos, talc, mica, slate, clays including kaolin, feldspar, quartz and magnesite and may have been derived from any one of the three primal types of rock; i. e., igneous, sedimentary, and metamorphic. They are divided into three classes with reference to their reaction; viz., acid, such as ganister and Dinas clay; neutral, such as fire clay, chrome, ironstone, and graphite; and basic, such as dolomite bauxite and alumina. It will be noted that where silicon dioxide ($SiO_2$) predominates, the refractory material is acid in character and where the content is low, the refractory is basic.

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**Ganister** is composed of $SiO_2$89.5, $Al_2O_3$4.8, FeO2.8, CaO.1, $K_2O$.1, $H_2O$2.2.

**Dinas Clay** = $SiO_2$98.3, $Al_2O_3$.7, FeO.2, CaO.2 $K_2O$.1, $H_2O$.5.

**Kaolin**, which is the purest form of fire-clay, contains $SiO_2$ 45-60, $Al_2O_3$ 33-40, $H_2O$ 11-14.

**Dolomite** = $CaCO_3$54.34 and $MgCO_3$45.66. In this case the carbon dioxide is removed by heat, leaving the oxides of calcium and magnesium, which are entirely basic.

**Bauxite** = variations: $Al_2O_3$ 30.3-76.9; $H_2O$ 8.6-31.1; $Fe_2O_3$, 0.1-48.8; $SiO_2$ 1.1-41.5; $TiO_2$, 1.6-4.0.

The purposes for which refractories are intended to be used determines their selection. Some are intended to withstand high and prolonged temperatures, some to withstand the scorifying action of the substances fused in contact with them, and in particular this determines their selection for crucibles, while others such as quartz are designed to withstand sudden and extreme changes in temperature. The fusing points of some of the more common refractories used as furnace linings are as follows:

| | |
|---|---|
| Common fire brick | 1555° C. to 1725° C. |
| Bauxite " " | 1620° C. to 1800° C. |
| Silica " " | 1700° C. to 1722° C. |
| Chromite " " | 2050° C. |
| Magnesia " " | 2720° C. |

**Crucibles.—These are vessels designed for calcining or fusing substances which require high temperatures.** A good crucible should be tough, infusible, capable of withstanding sudden changes of temperature without fracture, and should not be readily corroded by metallic oxides. The most infusible crucibles are those made with clays containing the largest amount of silica, and the smallest quantity of calcium and iron oxides. A good crucible may be made with two-thirds fire-clay and one-third burned fire-clay and coke dust, which prevents it being distorted when burnt. The power of resisting corrosion may be tested by melting copper in the crucible and adding a little borax. The latter unites

Fire-clays are essentially hydrated silicates of alumina, which resist exposure to high temperatures without melting or softening. They contain small amounts of lime, magnesium, oxide of iron, potash, etc., and some mechanically mixed silica, and should not fuse lower than 1500° C.

Graphite (Cumberland) = C91.55, volatile matter 1.1, ash 7.35.

*Hiorns.*

with any copper oxides that may be formed, and will corrode the crucible rapidly unless it is of good quality.

Graphite, black lead, or plumbago crucibles are made of fire-clay mixed with varying proportions (25 to 50 per cent) of plumbago or coke dust. The best ones are made with purified plumbago, as the natural material often contains impurities in the ash which would act injuriously in the clay. Instead of using black-lead crucibles, clay ones lined, or "brasqued" with charcoal paste are often employed. The graphite crucible is the most enduring of all crucibles, but it should never be used in melting or alloying noble metals without first being tested by subjecting it to a red heat, as a crack or other imperfection may exist that escapes the notice while the vessel is cold. Again, bubbles of air or particles of organic substances occasionally become mixed with the material, which upon being heated, cause the crucible to be broken, thereby risking the loss of the metal.

There are a variety of clay crucibles, the most important of which are: (1) **French**—Of excellent quality, smooth, carefully made, but somewhat brittle; (2) **London**—Close-grained reddish brown, refractory, and resist well the corrosive action of metallic oxides; (3) **Cornish**—Quite refractory, but are of a more acid character than the preceding, and hence are more readily attacked by metallic oxides; (4) **Hessian**—These are exceedingly useful refractory, not readily corroded. They are composed of $SiO_2$, 54 parts; $Al_2O_3$, 41 parts; CaO, 2 parts; $Fe_2O_3$, 1 part; and they have been made in Grossalmerode since the fifteenth century. They may be used for rough fusions, but when precious metals or their alloys are to be fused in them, they

should be first thoroughly lined with a surface of borax, or the rough, porous sides will absorb a considerable portion of the molten metal. Being of acid character, they are also subject to corrosion by basic fluxes, with which they form fusible compounds. They are well adapted to the fusion of noble metals where no fluxes are introduced for chemical action. Though they do not show a great resistance to extreme heat, they are very slightly affected by sudden alterations in temperature, as they may be plunged cold into a strongly heated furnace, or white-hot into cold water without cracking. The Cornish crucible, though very similar to the Hessian variety, is not quite so rapidly perforated by corrosive fluxes.

Crucibles are also made of porcelain, gold, silver, platinum, iron, etc., but their use is confined almost entirely to the chemical laboratory.

Platinum is fused either in a crucible of gas carbon or in a concavity carved in a block of quicklime, the latter of which forms part of the furnace described in the chapter on platinum.

**FLUXES are certain fusible substances which, when heated with metalliferous matter, assist in the fusion and aggregation of the metallic globules by cleansing and protecting them from foreign matters,** such as gangue, oxides, sulphides, chlorides, etc.

With these foreign substances the flux forms a fusible slag from which the metals held as oxides, sulphides, chlorides, etc., may be subsequently reduced.

Like the refractory materials, fluxes may be classified as *acid, neutral,* and *basic* in their reaction. Thus, when gold quartz is fused with sodium carbonate, the quartz, a siliceous or acid gangue, reacts with the

carbonate forming sodium silicate, liberating carbon dioxide, and separating the gold which is held mechanically.

A number of fluxes are used for the specific purpose of removing certain impurities or debasing elements from molten metals. This they accomplish in two ways—first, by acting as simple solvents for the impurity, as mentioned previously, and forming a slag; second, by forming compounds, such as oxides, sulphides, chlorides, etc., with the debasing elements, which are either volatile or soluble in the molten flux. Others act in a reverse manner; these are reducing agents, the function of which is to reduce to a metallic state such metallic oxides as are dissolved in the molten metal, and which confer friability or brittleness upon the metal when cast.

The following may be enumerated as the fluxes of most common application, with their uses defined:

**Borax,** sodium tetraborate, $Na_2B_4O_7$, $10H_2O$. This salt is of almost universal use, but should be first fused to drive off its ten parts water of crystallization, and the glassy mass thus obtained is to be powdered. When highly heated it is of acid reaction, combining with metallic oxides to form borates; at lower temperatures it takes up foreign matters generally, setting the metal free and so cleansing its surface as to allow of complete aggregation of the particles into a button form. It is found native in abundance in California, Europe, Peru, and other localities. It is also artificially prepared by neutralizing boric acid with soda ash.

**Sodium Carbonate,** $Na_2CO_3$, $10H_2O$. This salt may be preferred to potassium carbonate from the fact that the latter is quite deliquescent. It decomposes silicates,

as already instanced, and much easier when charcoal is present. It forms fusible compounds with metallic oxides and decomposes some chlorides, for example, silver chloride.

**Potassium Carbonate,** $K_2CO_3$, is quite similar to the sodium salt; it dissolves the earthy impurities, with which it forms an exceedingly liquid flux, thus enabling the heavier particles of metal to sink through the fluid mass and collect in a button at the bottom of the crucible.

**Potassium Nitrate,** saltpetre, nitre, $KNO_3$, is an exceedingly useful flux in the purification of noble metals. When used as a flux, and heated, it energetically gives up a portion of its oxygen to base metals which are thus oxidized, and the alkaline nitrate becomes a nitrite.

**Sodium Chloride,** NaCl, powdered and heated, to prevent its decrepitation, is sometimes added to molten substances which induce much ebullition in order to check the latter and protect the substance operated upon from the action of atmospheric oxygen. Like ammonic and mercuric chloride, it forms chlorides with some metals. It is the most reliable flux in fusing brass and should be put in the crucible at the beginning of the heat.

**Black Flux,** a mixture of potassium carbonate and pulverized charcoal, is an excellent reducing agent and assists in the fusion of substances.

**Lime, Silica, and Alumina,** or lime with the silicate of aluminum, are employed together; the silica to abstract certain bases by forming with them fusible silicates, while the two bases, lime and alumina assist in the fusion of the silicates thus formed. A single silicate with one base is generally less fusible than a double

or multiple silicate with two or more bases—hence the two bases, lime and alumina, are used with the silica.

**Plumbic, Cupric and Ferric Oxides** are used as fluxes in some metallurgic operations; the first forming an alloy of lead and silver; the copper oxide for purifying gold and the ferric oxide as a flux for silica.

Many prepared fluxes have been introduced from time to time for dental soldering operations, but none possess any great advantage over pulverized dehydrated borax.

A liquid flux used by jewelers and found useful in dental solderings is made by dissolving equal parts of borax and boric acid in about sixteen parts of water.

**FUEL.—Combustible substances that may be quickly burned in air, producing heat capable of being applied to economic purposes.**

Fuels are chiefly compounds of carbon and hydrogen, known as hydrocarbons. Most of them contain other elements, but are essentially carbon and hydrogen. If oxygen is contained, the proportion of hydrogen may be equal to, or greater than, but never less than that required to form water with oxygen.

**Calorific Energy.**—The amount of heat a unit weight of a body is capable of yielding when completely burned. It is usually measured by the number of the units of weight of water it will raise one degree of temperature Centigrade.

Thus in the subjoined table the calorific energy of wood charcoal, for example, is given as 8080, that is to say, one pound of wood charcoal when completely oxidized to carbon dioxide will yield sufficient heat to raise 8080 pounds of water through one degree Centigrade; so with the other substances composing the table.

*The calorific energy of a fuel containing carbon, hydrogen, and oxygen is the sum of the calorific energies of the carbon and that of the disposable hydrogen.**

The experimental and calculated calorific energies of substances do not agree. This is probably on account of the heat absorbed in their decomposition.

**EXAMPLE No. 1.**—Determine the calorific energy of marsh gas ($CH_4$).

$C = 1 \times 12 = 12$ (The atomic weight of carbon is 12.)
$H_4 = 4 \times 1 = 4$ (The atomic weight of hydrogen is 1.)

$CH_4 =$ 16 (The molecular weight of marsh gas.)

In one pound of $CH_4$ there is then $^{12}/_{16}$ or $^{3}/_{4}$ lb. of carbon, the calorific energy of carbon is 8080 (see table) hence: $^{3}/_{4} \times 8080 =$ 6060.0

In one pound of $CH_4$ there is $^{4}/_{16}$ or $^{1}/_{4}$ lb. of hydrogen, the calorific energy of hydrogen being 34462 ..... $^{1}/_{4} \times 34462 =$ 8615.5

Therefore the calculated calorific energy of marsh gas is ....14675.5

**EXAMPLE No. 2.**—Determine the calorific energy of olefiant gas ($C_2H_4$).

**EXAMPLE No. 3.**—Determine the calorific energy of ethine ($C_2H_2$).

**EXAMPLE No. 4.**—Determine the calorific energy of alcohol ($C_2H_5HO$).

**EXAMPLE No. 5.**—Determine the calorific energy of bisulphide of carbon ($CS_2$).

The calorific energies of different substances obtained experimentally, by the method mentioned previously, is given in the following table:

TABLE OF CALORIFIC ENERGIES

| | | | |
|---|---|---|---|
| Hydrogen ..... | Burned to water, $H_2O$..... | | 34462 |
| Carbon (wood charcoal) | " " Carbon dioxide, $CO_2$... | | 8080 |
| " " " | " " " monoxide, CO.. | | 2474 |
| Silicon ..... | " " Silicic anhydride, $SiO_2$. | | 7830 |
| Phosphorus ..... | " " Phosphoric anhydride, $P_2O_5$ ..... | | 5747 |
| Sulphur ..... | " " Sulphurous anhydride, $SO_2$ ..... | | 2140 |

*Disposable Hydrogen.—The amount of hydrogen which may be combined with oxygen is not available as a source of heat, and is called "non-disposable" hydrogen; the excess of hydrogen over the amount which may be combined with oxygen being available is called "disposable" hydrogen.

CARBON COMPOUNDS

| | | | | | | |
|---|---|---|---|---|---|---|
| Marsh gas, $CH_4$..... | Burned | to | $CO_2$ | and | $H_2O$ | .....13063 |
| Olefiant gas, $C_2H_4$..... | " | " | " | " | " | .....11857 |
| Illuminating gas, H, CO, $CH_4$, $C_2H_4$, $C_6H_6$, etc.. | " | " | " | " | " | about.....12000 |
| Crude petroleum ..... | " | " | " | " | " | .....10190 |
| Wax ..... | " | " | " | " | " | .....10496 |
| Tallow ..... | " | " | " | " | " | ..... 9000 |
| Alcohol ..... | " | " | " | " | " | ..... 7183 |
| Carbon monoxide ..... | " | " | " | ..... | | 2403 |

**Calorific Intensity** is the pyrometric degree of heat obtained when a substance is completely burned.

**Pyrometry** is the measurement of high temperatures, and is accomplished by means of an instrument called a *pyrometer.* There are several types as (1) Compounds which fuse at graded known temperatures; (2) Resistance, which depend on variations in the resistance of a thermo-electric couple; (3) Expansion, which is based on the difference in expansion between a steel tube and a graphite rod. They are seldom accurate and rarely used above 540° C.; (4) Optical, which utilize the changes in brightness of a heated object; and (5) Radiation pyrometers.

The first type is used chiefly in the ceramic industry and has little value in crucible or muffle work. Seger cones graded to fuse at differences of 20° in temperature are the common types. The second type depends on three factors, first, the amount of current; second, the constancy of the current; and, third, the ability to withstand the conditions under which it is used. Each instrument consists of three parts, the thermo junction, the leads, and the galvanometer. The thermo junction may consist of one platinum wire, and

one platinum 90%, Rhodium 10%, wire, joined at one end, or it may consist of an alloy of iron, nickel and aluminum coupled with an alloy of nickel chromium and copper. The Platinum Rhodium couple can be used to 1600° C. (2900° F.) and will withstand constant heating to 1480° C. (2700° F.), while the base metal couples will stand a constant use of 1090° C. (2000° F.). The leads are usually of copper of the same resistance for which the galvanometer is calibrated and the latter instrument is connected in series in the circuit and calibrated to read in degrees of temperature. This type is extensively used in the fusing of dental porcelain with considerable satisfaction especially where an automatic circuit breaker is included. The optical pyrometers are extensively used in foundries where large amounts of metal are fused.

**FUEL.**—The fuels used in dental laboratories are petroleum, gasoline, alcohol, acetylene, and coal gas.

**Petroleum.**—Kerosene or coal oil is one of the products in distilling crude petroleum, and is much used where gas is not available. Since most dental lamps and stoves are of metallic construction, due precaution must be exercised to use only good "high test" oil, i. e., that which has been properly freed from the volatile products of petroleum and is capable of withstanding the maximum temperature developed by the lamp-flame without evolving dangerously combustible gases. It has been found that 5 per cent of crude naphtha reduces the flashing point from 118° to 70° F.*

**Gasoline.**—A colorless, volatile, inflammable liquid;

*A quick method of determining a low flashing point is to pour about two c.c. of the oil to be used on the surface of a glass of water, and then pass a lighted match over the surface. If the vapor is lighted, the oil is too low grade for furnace work.

one of the products of the distillation of crude petroleum, having a specific gravity of .629 to .667 at 60° F. It is so volatile that if a current of air be passed through it at ordinary temperatures a highly dangerous combustible gas is formed by the mixture of gasoline vapor and atmospheric air. It is much used as a fuel in vapor stoves and for carburizing air-gases, etc., see Fig. 7.

**Alcohol.**—A colorless volatile inflammable liquid, chiefly obtained from the fermentation and distillation of saccharine fluids, as grape sugar, or the distillation of wood. The former is known as ethyl alcohol, the latter as methyl alcohol, and a combination of the two with some strongly odorous or bitter tasting combustible substance is known as denatured alcohol. Alcohol is miscible in all proportions with water, hence the possibilities of dilution are great. Those using the liquid fuel will find it to their advantage to use a U. S. Custom House hydrometer with Tralle's and Proof Mark scales to determine the alcoholic content of their purchases.

| | | | | | |
|---|---|---|---|---|---|
| 90% | alcohol | has | a | specific gravity | of 0.826 |
| 80% | " | " | " | " | 0.856 |
| 70% | " | " | " | " | 0.882 |

The heat of combustion of ethyl alcohol is nearly twice that of methyl alcohol and it is intensified by injecting a blast of air into the burner. Denatured alcohol is usually sold at about two-fifths the price of ethyl alcohol.

**Acetylene.**—Formula $C_2H_2$, obtained by the action of water on calcium carbide, is a volatile gas, easily compressed into liquid form and thus stored for convenient use. When a jet of oxygen or air is injected

into a blast lamp connected with an acetylene container and the mixed gases are ignited, a very intense heat is produced. This constitutes the oxy-acetylene welding flame, and the temperatures obtained are so high that the product is at present unsuited for dental laboratories. A modified type of burner and blowpipe will add a very useful fuel to the dental laboratory, since the condensed gas is easily obtained in convenient sized storage tanks now.

**Coal Gas.**—Illuminating gas as it is frequently called is a distillation product of the varieties of coal known as bituminous and cannel.

**EXPERIMENT No. 11.**—Fill the bowl of an ordinary clay pipe with small fragments of bituminous coal, lute over with clay and place in a bright fire; immediately smoke is seen to issue from the stem which projects beyond the fire. The smoke soon ceases, and if a lighted taper is then applied to the orifice of the stem, the issuing gas burns with a bright steady flame, while a proportion of a black, thin, tarry liquid oozes out from the stem. After the combustion ceases, there is left in the bowl of the pipe a quantity of char or coke.

This simple experiment is, on a small scale, an exact counterpart of the process by which the destructive distillation of coal is accomplished in the manufacture of gas. The products of this distillation process are classed in the gas works as gas, tar, ammoniacal liquor and coke. The gas is purified by removing the tar and ammoniacal liquor, and then passed into the pipes for consumption. It is composed of a variety of substances divided into two classes; viz., (1) *Nonluminous diluents,* embracing hydrogen (H), marsh gas ($CH_4$), and carbon monoxide (CO); (2) *luminous constituents,* which include the hydrocarbon gases acetylene ($C_2H_2$),

olefiant gas ($C_2H_4$), propylene ($C_3H_6$), butylene ($C_4H_8$), and most important of all the vapors of the benzol ($C_6H_6$), and the naphthalin ($C_{10}H_8$) series.

**REDUCTION OF ORES.**—Occasionally metallic ores are obtained in compact masses of comparatively pure metal, from which the accompanying matrix or gangue can be detached by the hand or hammer, but such instances are rare. In most cases the ore comprises but a small percentage of the gangue. Hence it is expedient to purify it as much as possible before attempting to liberate the metal. This is accomplished generally by crushing and washing out the earthy matter as far as practicable. The ore is then subjected to roasting, amalgamating, or dissolving operations for the reduction or liberation of the metal.

The great majority of metals are reduced by heat. In this process the ore, along with some kind of flux, is exposed to the direct action of a powerful fire, which in most cases has a chemical as well as a physical function. It is intended, with the assistance of the flux, to break up or burn away some chemical compound or component, or it is meant to deoxidize the ore.

For these fiery operations immense furnaces are constructed of brick, granite, or other building stone, and lined with refractory or fire-resisting clay, brick, etc.

**FURNACES** are best classified, by the method adopted for supplying air, into two classes; viz., (1) *blast furnaces,* (2) *chimney draught furnaces.*

**Blast Furnaces** are supplied with air from a source under pressure (*B'* Fig. 2) sufficient to overcome the resistance to its free passage presented by the packed columns of fuel, flux and ore. These are the oldest and simplest forms of metallurgic contrivance. The

open hearth blacksmith's forge is a simple type of the same principles involved in the completely closed-in

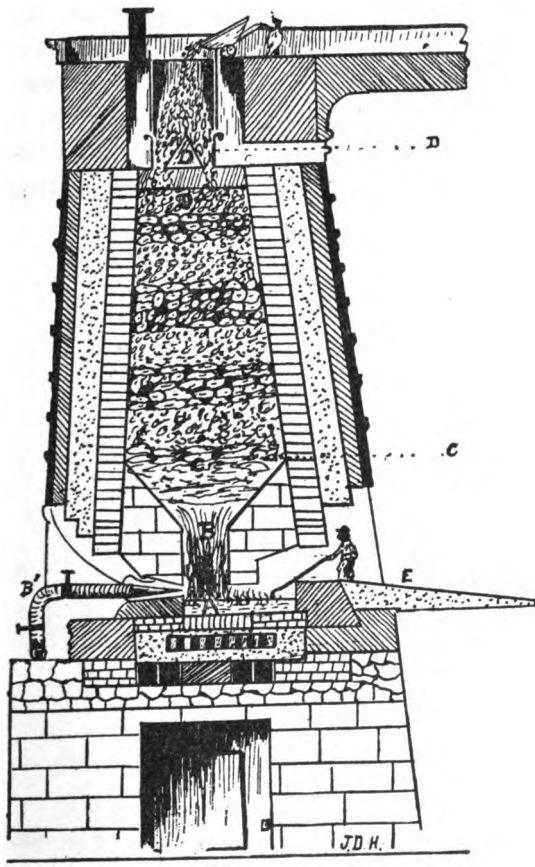



Fig. 2.—Sectional view of blast furnace.

blast-furnaces of gigantic dimensions* in use for work-

*In the Middlesborough district, England, is a furnace 103½ feet in height, and of 33,000 cubic feet capacity.

ing and reducing the various compounds of iron. Fig. 2 is a vertical section of a blast-furnace. The upper cone *D C* is known as the stack proper, the lower one from the broadest part *C* to the tuyères *B*, as the boshes, and the lower cylindrical part *A*, *B*, as the hearth.

**A Chimney Draught,** *Air*, or *Wind Furnace* is supplied with air drawn through it by a partial vacuum in the chimney formed by the heated gases on their way

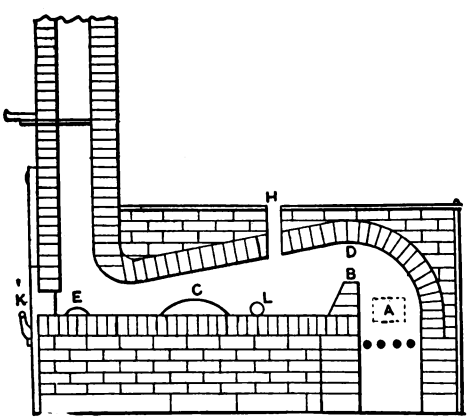



Fig. 3.—Reverberatory furnace.

to the atmosphere. The *reverberatory furnace* is a type of this class. Fig. 3 represents a vertical section of the reverberatory furnace.

The *characteristic point* in this furnace is, that the fire-chamber *A* is separate from the one in which the material to be operated upon is placed—the heat and flame passing over the charge as from *A*, *D*, *E*. *B* is a low wall dividing the fireplace from the working bed *C*, and is known as the fire-bridge. At the opposite end

there is sometimes a second bridge of less height called the flue-bridge, *E*. The ore is introduced from hoppers at *H*, the slag is withdrawn at *K*, and the metal run out by a tap hole at *L*.

For melting gold and silver, as for all ordinary melting operations, Mr. Makins recommends one after the style of Fig. 4, which is known as a crucible furnace. This may be built in an ordinary house-flue with a chim-

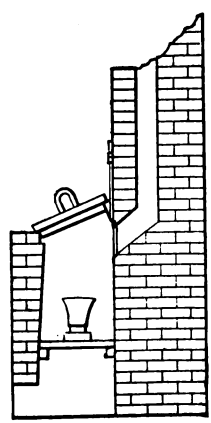


Fig. 4.—Crucible furnace.

ney whose height is about *thirty times the diameter of the furnace*—or thirty feet in height, for a furnace of one foot in diameter.

A third class of furnaces is known as *Muffle Furnaces*, and under this head are to be found the assayer's furnace and the *continuous-gum furnace*. The principle of these is the avoidance of contact of the substance heated with either fuel or flame. This is accomplished by the use of a muffle which is a chamber communicating with

the external air and into which the article to be heated is introduced. This chamber or muffle is placed in the combustion chamber, and is surrounded by the burning fuel but does not communicate with the combustion chamber. The electric dental porcelain furnace is of the muffle type modified, however, in that the heat is produced by the resistance of a given conductor to the passage of the electric current rather than by the combustion of fuel.

**Dental Laboratory Furnaces.**—For melting metals in the dental laboratory, the small, compact blast-furnace devised by Mr. Fletcher, and shown in Fig. 5, is the simplest and most convenient.

It consists of a cylindrical casing and perforated cover made of fire-clay which has been mixed with three or four parts by bulk of sawdust and burned. Through a hole near the bottom of the casing the mixed air and gas is injected, the latter being regulated by a check near the mixing chamber. The gas is received from as large a supply-pipe as convenient, and the air driven in by means of the foot-bellows. The crucibles used should not exceed 2 by 2¼ inches. According to Mr. Fletcher, "With half-inch gas-pipe and the smallest foot-bellows the smallest sized furnace will melt a crucible of cast iron in seven minutes, tool steel in twelve minutes, and nickel in twenty-two minutes, starting with all cold." Gold, silver, or copper may be readily fused in one of these furnaces where gas is accessible. Where gas is not convenient, the metals or dental amalgam alloys may be melted very satisfactorily in a near-by blacksmith's forge, or in a coke or coal fire in an ordinary stove or open fireplace if the draught is sufficiently strong. If the draught is weak,

the combustion of the fuel may be better accomplished by improvising a blast by passing a small piece of gas-pipe between the grate-bars of the fireplace or stove and attaching to this the hose from the foot-bellows.

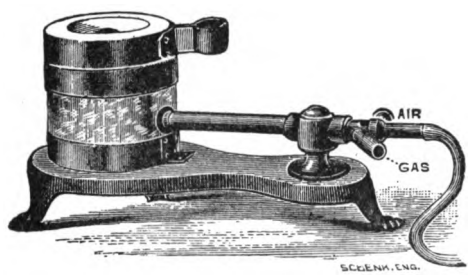



Fig. 5.

In this manner a considerable quantity of gold, silver, copper or alloy may be melted with little trouble.

A modified type of Fig. 5 has been devised (Fig. 6)

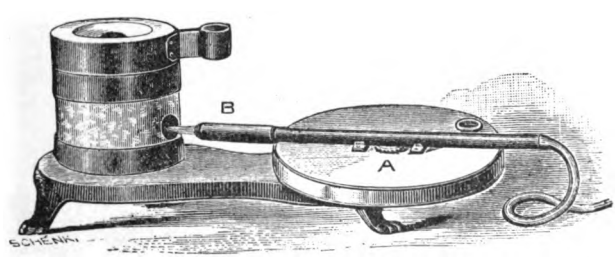



Fig. 6.

retaining all its peculiar advantages, but burning petroleum, instead of gas, as fuel. The burner dispenses with a wick, by being constructed on the principle of an atomizer. It is supplied with a device for regulating the supply of oil, which is operated by the milled nut at

*A*, and for the supply of an annular jet of air which is regulated by turning the sleeve *B*.

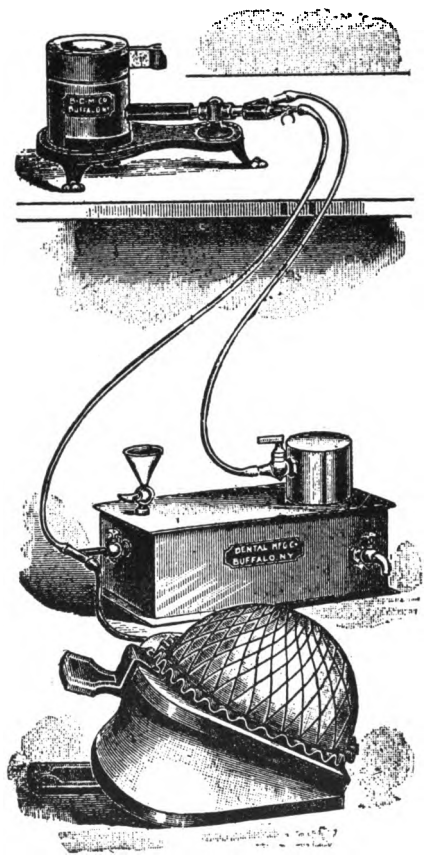



Fig. 7.

The construction is such that it may be taken apart and cleaned, in case of any obstruction. The furnace stands are interchangeable for either gas or petroleum.

Where illuminating gas is not attainable, a much more convenient form of furnace than that shown in Fig. 6 may be had as illustrated in Fig. 7. The gasoline generator placed beneath the bench is attached to foot-bellows and furnace.

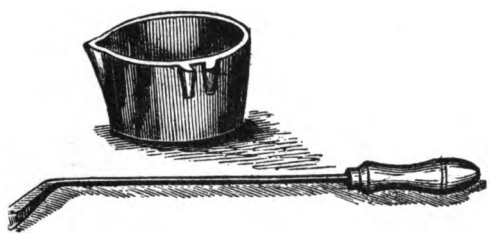


Fig. 8.

For those metals which fuse much before redness, such as zinc, lead, tin, and their alloys, iron ladles are usually employed. In the dental laboratory for melt-

Fig. 9.

ing zinc, lead, or alloys, for making dies and counter-dies, iron melting pots (Fig. 8), capable of holding from 6 to 10 pounds of metal, are used. The metal may be most conveniently melted over one of Fletcher's solid flame gauze-top stoves, shown in Fig. 9. The

stove is so constructed that the gas mixed with the proper proportion of air from below is burned above the gauze top, yielding a blue flame, intensely hot and perfectly solid and uniform. The consumption of gas is about two cubic feet per hour for each square inch of gauze surface. It will melt an ordinary pot of lead in 12 minutes, depending on the gas supply. An apparatus in which gasoline may be used, when gas is not available (much used by plumbers for melting solder), is recommended by Dr. Kirk* for melting zinc and lead in the dental laboratory. In the absence of gas supply it is probably more convenient to melt these metals in the open fireplace or in the stove.

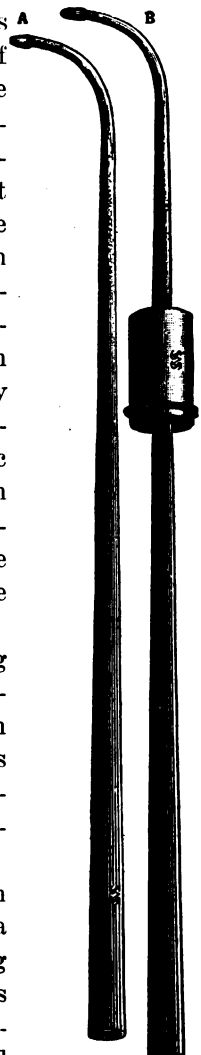


Fig. 10.

**BLOWPIPES.**—For minor melting operations, such as melting small quantities of gold, silver, or copper, or in soldering, the blowpipe in some of its variously modified forms is usually employed. These instruments are classified as *simple* and *compound.*

A *simple blowpipe* of plainest pattern is shown in Fig. 10, *A*. It consists of a tube of brass or other metal tapering gradually from the larger end, which is inserted in the mouth, to the other extremity, which is curved and mounted

*American System of Dentistry, iii, p. 816.

with a cone-shaped tip to protect it from the action of the flame; the caliber of the instrument terminates here in a very small orifice. The point of the instrument is frequently tipped with amore refractory metal, such as platinum, and the end to be received in the ment is frequently tipped with a more refractory metal, such as silver. The whole is usually from twelve to fourteen inches in length, and the large extremity from one-half to three-fourths of an inch in diameter.

As more or less moisture accumulates in the tube from the mouth, a second form has been devised (Fig. 10, *B*), to the stem of which, nearer its smaller extremity, is adjusted either a spherical or cylindrical

Fig. 11.

chamber, which collects and retains the moisture as it forms within the pipe. The moisture is prevented from flowing into the smaller end of the tube beyond by the projection of that portion of the stem a slight distance into the chamber.

Fletcher has much improved this simple form of blowpipe by coiling the smaller extremity of the stem into a light spiral over the point of the jet (Fig. 11). The air as it traverses the coil is heated, producing a hot blast instead of a cold one, as in the old form. Such an instrument enables the operator to produce a higher temperature than that produced with the ordinary pipe with the same amount of energy. The same pipe may be fitted with a hard rubber mouthpiece, which is less tiresome to grip in the mouth.

Another form by the same inventor is illustrated in Fig. 12. This is wholly unlike any mouth blowpipe yet devised, and admits of considerable latitude of movements in the application of heat by the rubber tubing connected with it. The mouthpiece is so constructed that a shield protects the lips in such a manner that long-continued blowing may be practiced without undue strain on the lips, while the opening is well under the control of the tongue. It is also provided with a condensing chamber and interchangeable tip, either plain or coiled.

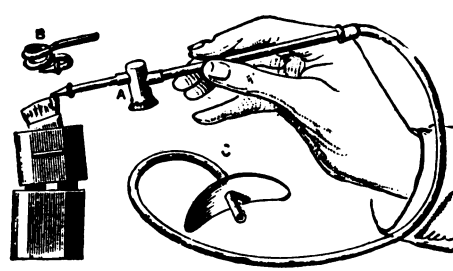



Fig. 12.

**Heat.**—In the dental laboratory heat is obtained either from the combustion of fuel or from electric energy, the former being its commoner source. Solid fuel, as coal or coke, is no longer in use, having been succeeded almost entirely by either liquid or gaseous fuel. Alcohol, gasoline, and kerosene are the liquids used for this purpose, the gas is commonly either ordinary illuminating gas or natural gas in those regions in which it is available. These all owe their inflammability to the fact that they are hydrocarbons, combustion of which takes place when they are heated

in air. One of the phenomena of combustion is the production of flame, which is simply burning gas.

**Flame.**—The simplest flames with which we are acquainted are those of hydrogen or carbon monoxide burning in air or oxygen. In such as these the burning gas undergoes no decomposition. The combustion consists of the simple union of an inflammable gas with oxygen:

$$H_2 + O = H_2O. \qquad 2CO + O_2 = 2CO_2.$$

The flame of either of these gases burning from the end of a tube appears as a burning cone, which upon investigation is found to be hollow, the combustion only taking place on the surface of the cone where the inflammable gas is mixed by diffusion with the air.

Substances which undergo decomposition and yield more than one product of combustion present a more complex flame structure. The flames of hydrocarbons commonly employed for illuminating purposes, such as the candle, illuminating gas, and oil, are practically identical in points of construction and a description of one will suffice for all.

**The Candle Flame.**—On approaching the wick with the flame of a match, the wax (or other hydrocarbon of which the candle may be made) melts, is drawn up in the fibers of the wick by capillary attraction and there converted by the heat into gaseous hydrocarbons, which ignite, and in their chemical union with the oxygen of the air produce the flame. In such flames, as in the simpler ones already referred to, there is first, about the wick or burner, the dark cone, *A*, of heated unburned gases. Above and about the apex of this cone is a second cone, *B*, which in comparison with the rest of

the flame, seems nearly opaque, and which emits a bright yellow light. At the base of the flame there is a small calyx-like region, *C*, which appears bright blue in color and is nonluminous. Then enveloping the entire flame there is a faintly luminous, hardly perceptible, bluish-purple mantle, *D* (Fig. 13).

*The dark cone, A,* as has been explained, consists of unburned gases and in reality is not a part of the flame. However, chemical changes are taking place

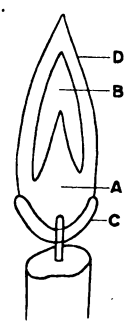



Fig. 13.—Candle flame.

therein, owing to the heat from the sheath of combustion surrounding it.

*Cone B* is ordinarily spoken of as the *luminous cone.* It has probably been concluded that the luminosity in flame is due to: (1) *the presence of solid matter,* (2) *the density of the flame gases* and (3), *the temperature of the flame.*

*The blue region, C,* may be regarded as being largely made up of the combustion of carbon monoxide.

*The faintly luminous mantle, D,* is probably a zone of complete combustion, in which those substances

which have been incompletely oxidized in the other portions of the flame, chiefly hydrogen and carbon monoxide, are finally converted into water and carbon dioxide.

**The Bunsen and Blowpipe Flame.**—When a certain amount of air is mixed with coal gas or any other

Fig. 14.—Bunsen flame.

hydrocarbon gas before combustion, the gas burns with a pale blue, nonluminous, smokeless flame, which has a three-cone structure (Fig. 14).

*Cone A* contains the mixture of combustible gases and air (oxygen). In the Bunsen burner the air is drawn in through the openings near the base of the metal tube. The mouth blowpipe conveys a blast of air into the

center of the flame. In the compound blowpipe flame the blast of air (oxygen) is injected into the combustible gases from the lungs of the operator or by some mechanical means, such as a bellows, through a concentered tube, while the gas is conveyed by the outer and larger tube (Fig. 15).

**The Reducing Flame,** (or deoxidizing flame).—The inner cone, *B*, presents the gas burning with a pale-blue flame, rendered so by the presence of oxygen in the gas. If an oxidized piece of copper be placed in a Bunsen or blowpipe flame in the position of the line marked *B' B'*, it will be noticed that the metallic sheet brightens in

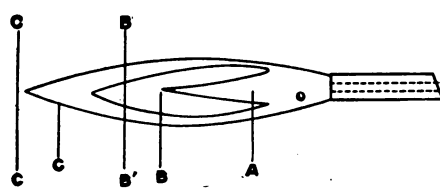



Fig. 15.—Blowpipe flame.

the area covered by the flame. This is accounted for by the fact that this region of the flame contains highly heated but unburned hydrogen or hydrocarbons, which have the power to abstract and then combine with the oxygen of the copper oxide, thus freeing or *reducing* the copper; hence, this region is known as the *deoxidizing or reducing flame.*

This is the flame used for soldering, as it reduces any oxides that may be on the solder, or parts to be soldered, and, also cutting off the oxygen of the air from contact with the heated metals, it prevents any reoxidation of them.

**The Oxidizing Flame.**—The outer cone, *C*, presents a pale-blue or purple color and is the zone of complete combustion. Gases which have escaped combustion in the inner cone are oxidized in the outer one by the ample supply of oxygen in the atmosphere surrounding it.

A bright piece of copper held in the position of the line *C′ C′* will be quickly darkened by the formation of copper oxide upon its surface. This is accounted for by the fact that the copper becomes heated, and, being unprotected, is unable to resist the affinity of the oxygen in the air surrounding it, and is therefore oxidized. Hence, the term *oxidizing flame.*

Any attempt at soldering with this flame results in oxidation of the base metals of the solder and parts to be soldered, so that additional fluxing will be necessary before the solder can flow. Continued misuse of the flame may so greatly raise the carat of the solder, by oxidizing out the base metals, as to make its fusing point dangerously high, or the presence of the oxides mixed with the solder may make its flowing impossible.

Because of the chemical nature of combustion, it is evident that the proportion between the air and the gas must be definite and fixed to obtain the highest heat, and this must be regulated when the blowpipe is in use. If too little air is supplied, imperfect combustion takes place and the full degree of heat is not developed. On the other hand, the luminosity of the flame is increased, the heat being inversely related to this. If too much air is forced in,* the temperature of the flame must nec-

*The best mixture of coal-gas and air is 1 part gas to about 5 or 7 parts of air by volume. It is better to mix the air and gas before combustion.—Sci. Am., Feb. 6, 1909.

essarily be reduced by the current of cool and uncombined air.

**Reduction on Charcoal.**—Reduction is much more easily effected by the employment of a block of charcoal as a support. It not only assists in heating the bead of metal by becoming hot, but it also assists in the reducing action by combining with the oxygen of the oxide, forming carbon dioxide, and liberates the metal.

**LAMPS.**—Flames for soldering may be derived from *oil, spirit,* or *gas lamps.*

**Oil Lamps.**—The fluid hydrocarbon, petroleum, or

Fig. 16.

coal oil is very inexpensive, and where gas is not available is much used. Fig. 16 represents a soldering lamp. An oil lamp to be satisfactory should hold about one to two pints and should have a tapering spout from three to five inches in length. The spout should be well filled with wick, but not too tightly, for fear of preventing free saturation with the oil. Proper care should be exercised to guard against all accidents occasioned by ill-fitting parts, filling and adjusting. With a good lamp, an entire artificial denture can be soldered, or one or two ounces of gold melted. Pure sweet

oil or lard oil may also be used in these lamps for soldering.

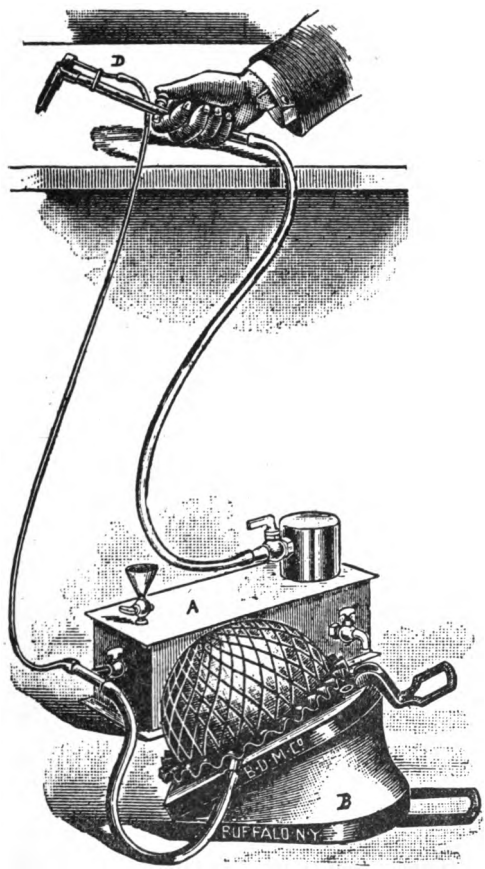



Fig. 17.

Fig. 17 illustrates a *compound blowpipe* (*D*) used with gasoline gas. It is provided with a generator (*A*)

and bellows (*B*) with which it is connected (*C*) similarly to that in Fig. 7.

**Spirit Lamps.**—Much the same lamps, as illustrated

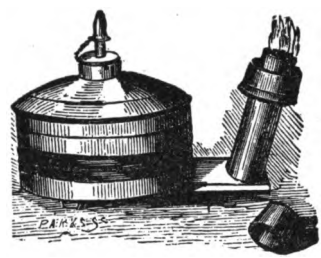


Fig. 18.

in Fig. 16 may be used for alcohol, which is much preferable to coal oil on account of its cleanliness and the less liability to accident. With a lamp similar to

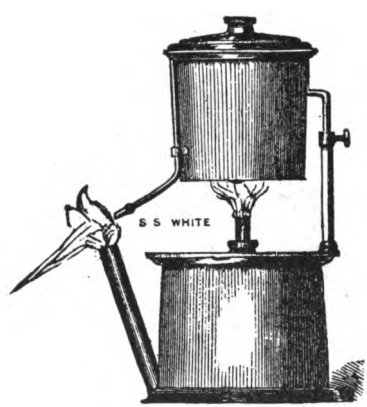



Fig. 19.

the one represented in Fig. 18, the spirit is entirely uninfluenced by the heat of the flame, and explosion is rendered almost impossible.

In Fig. 19 is represented a self-acting lamp and blow-

pipe. The lamp reservoir and the boiler will each hold about a half-pint of alcohol. Lighting the flame under the boiler vaporizes the alcohol in it rapidly, the pressure forcing the vapor through the pipe into the large flame at the side of the lamp, forming a very practicable

Fig. 20.

and efficient blowpipe. The force of the blast is regulated by raising or lowering the boiler; the spread of the flame by using the larger or smaller nozzle. The appliance is substantially made of spun brass, and the boiler is provided with a safety-valve. A set screw on

the upright permits the boiler to be raised or lowered or swung to one side. One of the nozzles is carried on the top of the safety-valve; the other in position on the pipe.

**Gas Lamps.**—The gas may be most effectively used by an apparatus on the principle of the one illustrated

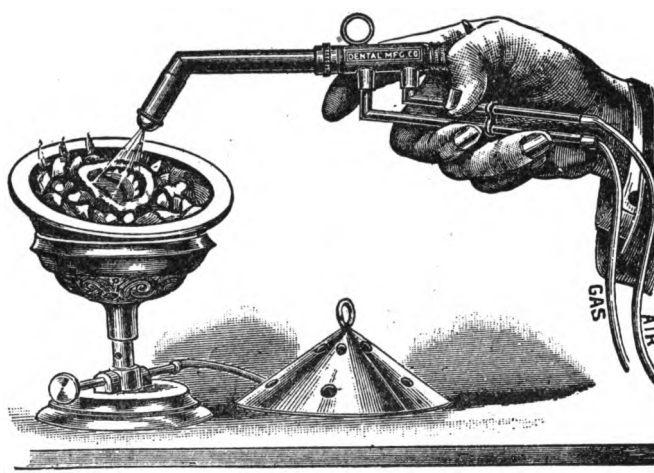



Fig. 21.

in Fig. 20, which consists of a sort of Duplex Bunsen burner.

**Compound Blowpipes.**—The difficulty in maintaining a flame of uniform size and intensity, owing to the fact that the blowpipe and lamps are separate, the lack of latitude allowed the operator by the fixed position of the blowpipe, and the introduction of gas in the experimental laboratory led to a form known as the compound blowpipe, Fig. 17. This instrument is so constructed that it virtually consists of a lamp and

blowpipe all in one. In general it consists of two metallic concentric tubes, one a smaller, terminating in a fine jet and placed within the first, so that the finer jet is accurately centered in the orifice of the larger tube, Fig. 21. Gas is supplied to the larger tube by an offset tube on the side of the nearer end, and flowing through the space in the large tube on all sides of the enclosed smaller tube to the opposite end, where it is ignited. Air from the lungs or other source is transmitted through the inner tube to the center of the

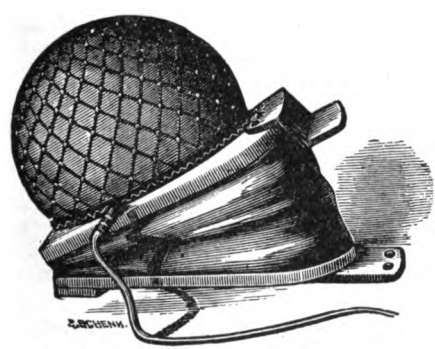


Fig. 22.

flame. The supply of both gas and air may be regulated in most of the latter patterns by checks within reach of the fingers of the same hand holding the instrument. The blast from the mouth is most convenient for small heating, but when high temperatures are desired for some time, one of the various forms of mechanical blowers is necessary. A far more satisfactory apparatus is found in the foot-bellows devised by Mr. Fletcher and shown in Fig. 22.

**SUPPORTS.**—When soldering or melting gold or

silver with the blow-pipe flame, it is necessary to place the article to be soldered, or the metals to be melted, upon some sort of a support. Such supports may be improvised of blocks of charcoal, if the temperature is not to be too high, or large blocks of pumice stone encased in plaster, giving the whole a variety of forms. One, designed by Professor C. L. Goddard which the author uses very comfortably, was made by making a mold of a hemisphere from a smooth croquet-ball, by pouring some plaster of Paris into a pasteboard box

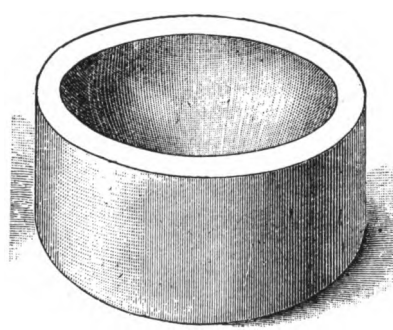


Fig. 23.

about five inches square, and then dipping the ball, and removing it when the plaster had hardened. The mold thus made was then varnished and filled with soft plaster, on the top of which was imbedded a large piece of pumice stone. When this hardened, the hemisphere was separated from the concavity, and the block containing the latter cut down until it covered but little over half of the hemisphere, when it was reinserted. The whole was then varnished, and presented a very compact, convenient soldering block, fitted in a

socket which permits it to be poised at almost any angle.

Blocks of charcoal may also be covered on all sides but one with about one-half inch thickness of plaster. They then furnish clean and convenient supports for small solderings and meltings.

Fig. 23 forms a convenient asbestos soldering-block, and Fig. 24 represents another more easily handled. The block is of carbon and is furnished with a wooden handle. Fig. 25 represents a circular asbestos soldering-block or tray, with raised rim, set in a brass box, mounted on a wooden handle. The four holes are for

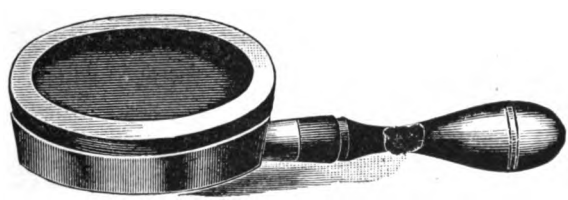


Fig. 24.

the reception of brass pins, to hold the work in place. The investing material is made of a prepared asbestos fiber. This material is simply dampened. When the objects to be soldered consist in part of artificial teeth, such as a denture or bridge, a support of the style of Fig. 26, a small hand-furnace or soldering-pan is very satisfactory. It consists of a funnel-shaped receptacle made of sheet iron, with a light grate or perforated plate of the same material adjusted near the bottom, and an opening on one side, underneath the grate, for the admission of air. The upper part of the holder is surrounded by a cone-shaped top, which may be readily

removed by a handle attached to it, while to the bottom of the furnace is attached an iron rod, 5 or 6 inches in length, enclosed in a wooden handle at its unattached end; when the case is sufficiently heated,

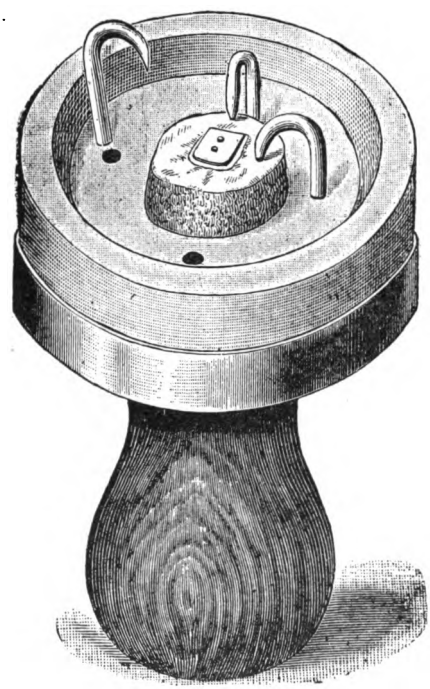


Fig. 25.

the top may be lifted off, and the case remaining in the furnace soldered with the blowpipe in the usual manner, the furnace then serving the place of a support.

**INGOT MOLDS** are usually made of iron in various forms to suit the requirements, those for the noble

metals generally having the form shown in Fig. 27, which is so constructed that the side next to the handle, which also acts as a set-screw, can be moved laterally upon the opposite side, so that the intervening slot may be made narrow or wide. Ingots are also frequently cast into molds of sandstone, charcoal, compressed carbon, pumice stone, or asbestos preparations.

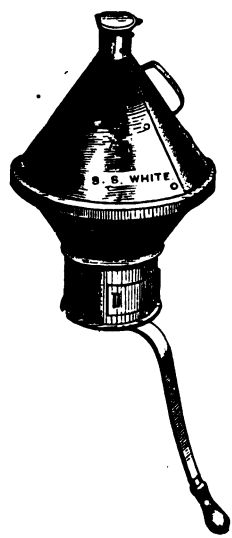



Fig. 26.

Fig. 28 represents such an apparatus suitable as a support for melting, and as an ingot mold for the molten metal by merely tipping the slab and placing a cold, flat surface over the still heated metal in the mold. It is very important to have the mold free from moisture before pouring the molten metal in it, since the sudden generation of steam may scatter the metal, causing a loss or perchance producing serious burns.

Fig. 29 is an arrangement for melting and molding noble metals without the use of a furnace. Referring to the engraving: *A* is a crucible of molded carbon supported in position by an iron side-plate. *C* the ingot mold. *D* a clamp holding the crucible and ingot mold in

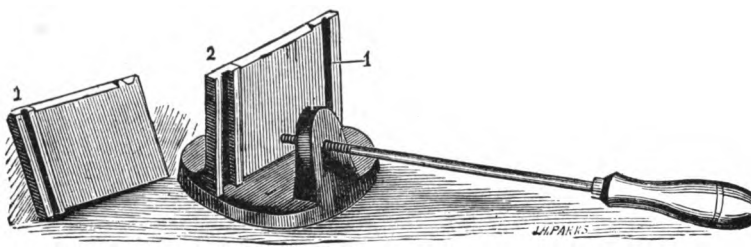



Fig. 27.

position, and swiveling on the cast iron stand *B*. The metal to be melted is placed in the crucible *A*, and the flame of a blowpipe is directed on it until it is per-

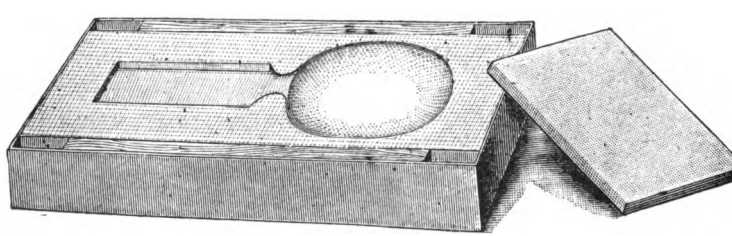


Fig. 28.

fectly fused. The waste heat serves to make the ingot mold hot, and the whole is tilted over by means of the upright handle at the back of the mold. A sound ingot may be obtained at any time in about two minutes.

**ELECTRIC FURNACES.**—These are of two distinct types. (1) The arc furnace and (2) the muffle furnace.

The arc furnace is employed principally for the reduction of metals from their ores and for the compounding of alloys requiring a high temperature. They are based on the principle of feeding the ore, flux and reducing

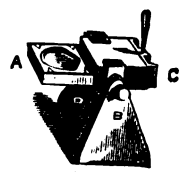


Fig. 29.

agent around the electrodes to close a circuit. The heat generated by passing the current through this charge raises the temperature and fuses the mass, thus reducing the ore. (Fig. 30.)

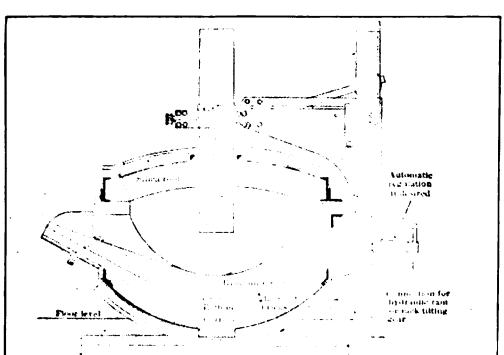


Fig. 30.—Grönwall type of electric arc furnace of two and one-half tons capacity. One carbon electrode is inserted in the base and the other in the top. When the steel is molten the furnace is tilted and the metal poured into ladles for casting.

Where fuel is scarce and hydroelectric energy is available in the neighborhood of ore deposits, electric reduction furnaces are very practicable. Only one-third

as much carbon in the form of charcoal or coke is required in electric furnaces since it is only required as a reducing agent, the electric energy through the resistance of the mass producing the heat. They may be used for the smelting of certain alloys because they can be easily controlled and being of a smaller type than blast furnaces are suited for smaller charges. Nearly all the ferro alloys are now made in electric furnaces.

Every dentist should be able to do porcelain work and since this requires a muffle type of furnace and the electric dental furnace is the cleanest and most practicable, one ought to understand the simple underlying principles of its construction so that if necessary a furnace could be repaired or reconstructed in a short time to meet any emergency.

The furnace consists of a rheostat and muffle connected in series. The rheostat is merely one or more resistance coils in series which will enable the operator to regulate the strength of the current passing through the furnace. Resistance is that property of a conductor which inhibits or modifies the current passing through it and is due to the composition, form, and molecular structure of the conductor.

Since resistance to the passage of the current produces heat, it is necessary that the coils have a high fusing point. Resistance coils in rheostats are usually made of iron or some of its alloys, with copper, nickel, and chromium predominating. The construction of an electric furnace is a requiremnet in the College of Dentistry, University of California. The type used is described and illustrated in the following pages. The base is of cast iron in three parts, the bottom and sides

being cast in one piece, the ends being separate and removable. Plenty of space for the circulation of air is provided so that the resistance coils will cool by radiation. (See Fig. 31.) The base carries five tin tubes one inch in diameter which fit at either end over slightly tapering projecting rings on the inner side of the cast

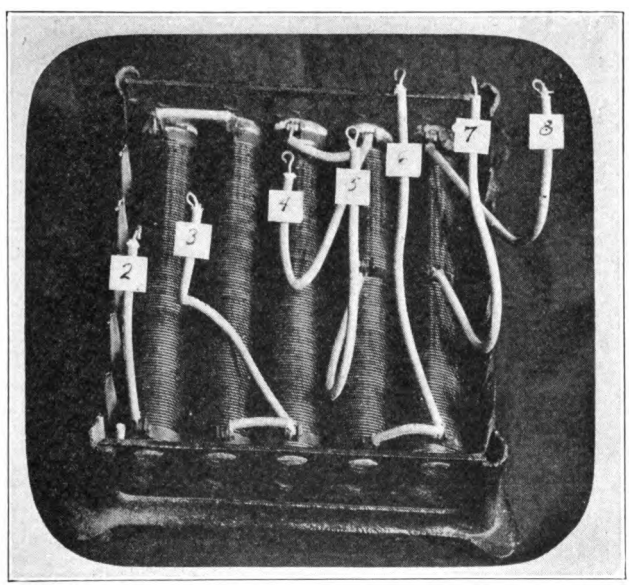



Fig. 31.

ends. Air passes freely through the hollow tubes to aid in cooling the rheostat. Each tube is covered with sheet asbestos fastened with shellac or fine iron wire and then the tube is wound with 20-gauge tinned iron wire, the ends being soldered to the last coil to prevent unwinding. (See Fig. 32.) In addition to this soldered joint a brass strap is formed tightly around

the end of each resistance coil and fastened with a very small stove bolt $\frac{1}{16}$x$\frac{1}{2}$ inch. Should the solder become fused by the heat generated in the coils, the clamp will prevent its unwinding. This clamp, by adding another washer and a lock nut, serves as a convenient aid to connect the alternate ends of the

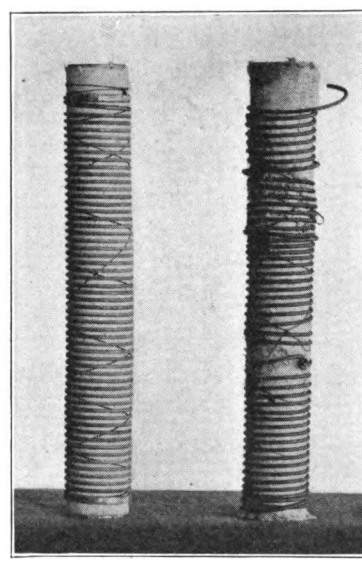


Fig. 32.

coils with one another, or for attaching a conductor to the middle of a coil as in No. 5, and No. 7, Fig. 33. A marble slab, 8$\frac{1}{2}$x9$\frac{1}{4}$x$\frac{7}{8}$ inches drilled as represented in Fig. 34 together with the necessary binding posts, contact points, etc., completes the rheostat. The four holes at corners are for the long stove bolts used to clamp the slab to the base and the four screws with

no conductors attached are to fasten the muffle base to the slab.

*A* and *B*, Fig. 34, are the binding posts to which are connected the leads from the source of electrical energy. (See also Fig. 38.) *C* and *D* are the connecting posts for the muffle terminals while *L* is the base of the lever bar. The resistance coils are connected by

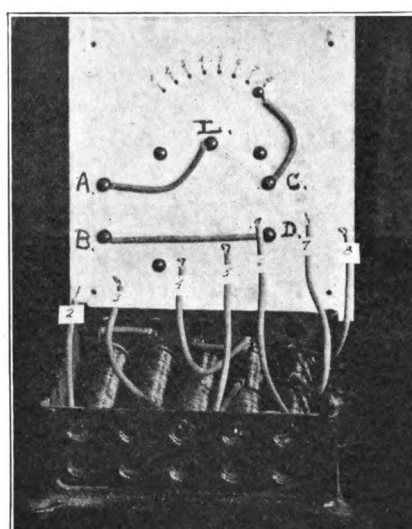



Fig. 33.

means of asbestos insulated wire to the corresponding numbers of the contact buttons. (See Fig. 33.) No. 1 button is always left with no conductors attached, thus serving as a dead button or a cut-out switch. In all rheostats it is the usual custom to cut out fifty per cent of the resistance with the first throw of the lever bar, and the next cut-out includes fifty per cent of the

remainder of the resistance. This is approximated as follows: When the muffle and rheostat are connected and the current is on, with the lever bar on button No. 1, no current is passing through the furnace, since this is a dead button. When the lever bar is moved to button No. 2, the current flows from binding post *A* (Fig.

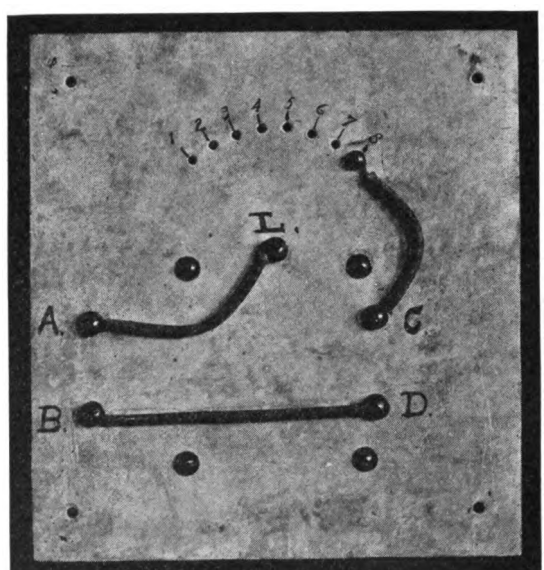



Fig. 34.

33) to *L* (lever bar), to button No. 2, to wire No. 2 to the first resistance coil, through all the resistance coils to wire No. 8, to button No. 8, to muffle terminal *C*, through the muffle to terminal *D*, to binding post *B*, and back to its source.

When the lever bar is moved to button No. 3, two

resistance coils or two-fifths of the resistance is cut out (see Fig. 31) and when the lever bar is moved to No. 4, another coil or three-fifths of the resistance is cut out. The remaining numbers 5, 6, 7, 8, cut out one-half a coil each. When the lever bar is on No. 8, the current is flowing only through the muffle, the rheostat being cut out entirely. It is well to state that in this or any other electro-heating device using a metallic resistor, it makes no difference whether the current is flowing from *A* to *B* or from *B* to *A*, if a direct current, or flowing either way at the rate of 60 cycles per second, if an alternating current. The utility of such a device depends entirely on the resistor and not upon the direction of flow of the current.

It is well to dip the resistance coils in shellac to prevent the oxidation of the metal but this coating of shellac should be scraped off wherever contacts are to be made. Climax and other kinds of resistance wire have been tried out in the resistance coils, but crystallization and oxidation undoubtedly aided by the passage of the current causes a number of breaks in the wire which may cause trouble at any time. When the conductors from the resistance coils are connected to the proper contact buttons and the marble slab securely fastened to the iron base, we are ready to proceed with the muffle.

The muffle case is of cast bronze 3x3¼x3 inches milled and buffed. It consists of two parts, viz., a base with four legs screwed to the marble slab. Near the muffle terminals two holes are drilled through the base which carry refractory insulating tubes through which the muffle leads pass to the terminals. The other part is a cap carrying a shelf at the base of door.

This cap is fastened to the base by two machine screws on either side. After the muffle is made, it is carefully packed in this muffle case with dry fibrous asbestos or magnesite so that the floor of the muffle is on a level with the shelf, the muffle leads are then passed through the insulating tubes, and connected to the terminals, the cap fastened to the base, and the completed furnace is ready for use. (See Fig. 38.)

**Muffle.**—The muffle is the most important part of the furnace and care should be used in its design and construction. The important thing to consider is to obtain the maximum amount of heat uniformly distributed with as little loss by radiation as is possible. The size of the muffle may vary to suit the needs or inclinations of the maker. The muffle used in this furnace is D-shaped, one and one-half inches wide, one and one-eighth inches high and two and one-half inches long. It may be made by taking a split wood, wedge shaped, pattern, or core of the desired size, from two to four inches longer than the muffle for convenience in handling, and covering it with glazed or waxed paper held in place by pins. The split wedge shaped core allows the center part to be easily drawn away when the sides will collapse, and thus allow the removal of the paper. Ten feet of 28-gauge platinum wire is used as a resistor and it has been found to meet all the requirements in fusing 2560° F. S. S. W. body. Beginning at one end near the muffle terminal side, the wire is fastened to one of the pins allowing about four inches for a two ply connection to the terminals, and is then wound around the core about one and one-half millimeters apart at the ends and about two millimeters apart in the center until the other terminal is

reached with another allowance made for a two ply terminal at the end. The object of folding about two inches of the platinum wire back upon itself and twisting it, is because it decreases the resistance gradually instead of suddenly and there is less danger of a burn out.

One may carve a block of plaster of Paris of the desired shape and size and then make shallow grooves

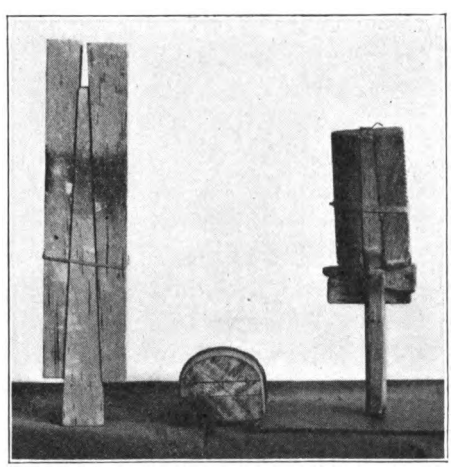


Fig. 35.

or scratches longitudinally in it, after which the platinum wire may be wrapped around it just as with the wooden core.

The wire is now ready to be coated with a refractory material which will resist high temperatures without change of form, and have no bad effect upon the platinum. Various combinations of silex, fireclay, ground firebrick and asbestos have been discontinued and an

artificially prepared refractory is now used with very satisfactory results. It is alundum R. A. 162, a high grade aluminum oxide to which has been added a binder to hold the mass together while molding or compressing into shape. The powder is moistened with water just enough to mold it easily and then applied to the core, covering the wires to a depth of one-sixteenth of an inch, gradually drying the muffle near a Bunsen flame as the alundum is applied. When completed and the ends are squared up, the muffle is dried out until it becomes set enough to withdraw the wooden core and paper, after which the muffle is heated to redness in the Bunsen flame. If a plaster core is used, it can be placed over the Bunsen just as soon as all volatile moisture has passed off and then heated to redness. Care must be taken not to heat a moist core over a flame too quickly as the steam generated within the core may explode and damage the entire mass. The plaster core will contract sufficiently with this heat to permit of its being withdrawn easily. The inner surface of the muffle should now be carefully examined for checks, or exposed wires and these places should be coated with the alundum paste. The muffle is now connected up with a rheostat and the current turned on until it produces a white heat. This hardens the alundum muffle and permits of its being handled with only ordinary care.

Alundum is a much better conductor of heat than other types of refractories and one should take precautions to see that none of this heat is lost by radiation. Therefore, an infusible nonconducting refractory is desirable to insulate the muffle from the outer air. If possible an air space should be provided between

these two materials, since dry air is the best nonconductor obtainable. Fibrous asbestos of a good grade that is not combined with siliceous compounds or binders used in the making of asbestos paper or felt is very satisfactory. Silicon or carbon in any of their forms should not be placed in contact with platinum when it is heated to high temperatures, since they combine quite readily with the latter and favor crystallization of the metal. Fig. 36 shows different types of muffles. No. 1

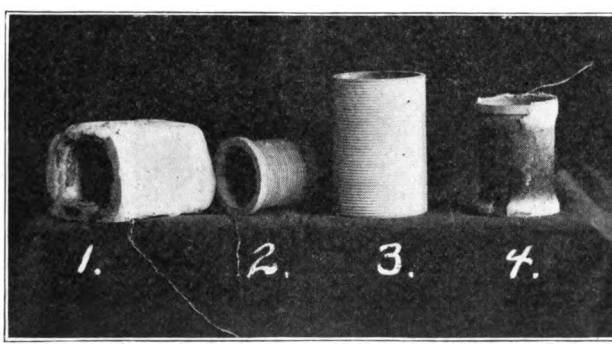



Fig. 36.

is the ordinary fireclay-silex mixture. No. 2 is an alundum tube with an additional concentric ring of the same material at either end. This was prepared so that the wire could be wrapped around the outside of the tube and then asbestos paper wrapped about the tube, allowing for an air space, as an insulator. It was unsatisfactory, first, because the bottom and sides were curved, and, second, the asbestos fused and when it came in contact with the heated platinum wires, it produced a short circuit and the wires were burned out as in No. 4. No. 3 is talc grooved while in the

natural state, and then subjected to a high temperature to vitrify it. It can not be turned or milled thin enough to permit of the passage of heat from the coil to the inside of the muffle and it is a very poor conductor as compared with alundum. Fig. 37 is the type of muffle adopted for use in this school. It simplifies construction and repairs very materially. The wire is wrapped on the outside in the grooves, the ends fastened securely, the muffle placed in a case surrounded by magnesite or fibrous asbestos and fireclay molded so that there is a definite air space about it, terminals

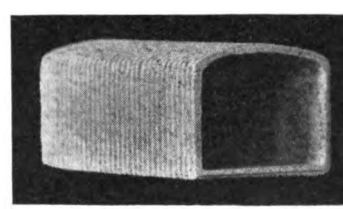


Fig. 37.

connected and it is ready. In the event of a burn-out, it can be removed, the ends electro welded or twisted together, and replaced very quickly. Fig. 38 shows the completed furnace without the muffle in place. The door to the muffle should be closed with a block of asbestos and alundum, one-half inch thick, formed to fit the opening with a convenient spur for handling with the furnace tongs.

A number of different substitutes for the platinum coil have been tried but none have proved to meet all the requirements. Nickel wire when protected from the air will give service up to 1000° C. Nichrome and French armor plate wire have been successfully used

at about the same temperature, but none of these elements or alloys will produce the heat required to fuse porcelain, viz., 1260°-1450° C. Tungsten is capable of producing satisfactory temperatures, and is much less expensive than platinum but is very easily oxidized at high temperatures. In an atmosphere of hy-

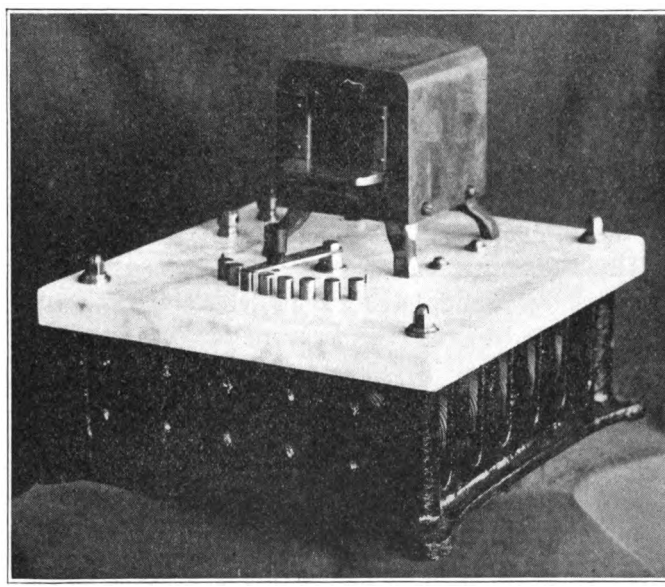


Fig. 38.

drogen it is very satisfactory, but it is impractical to set up a hydrogen generator in a dental office every time one wants to fuse porcelain. The resistance offered by any electrical conductor to the passage of the current is directly proportional to its length and inversely proportional to its cross-sectional area. It is obvious therefore that the shorter the length of wire,

the less heat will be produced within certain limitations. Further, the resistance of any conductor varies with the temperature, and this is known as the "temperature coefficient." The resistance of platinum wire increases 0.0025 with every degree Centigrade.

In using the older furnaces the workman had to depend solely upon visual judgment in determining when the porcelain was properly fused. Some made use of a pellet of pure gold, in working with the high-fusing bodies, placing it in the muffle and keeping the piece of work in the heat a definite time after the gold was seen to fuse (1060° C.). This principle is utilized by Le Cron in his pyrometer, in which by varying the proportions of gold and platinum in his pellet, the temperature of any given one of the high-fusing bodies may be judged, and, having been determined, the body may be baked at that temperature.

## CHAPTER V

## ALLOYS

**AN ALLOY is the compound or mixture of two or more metals effected by fusion.**

**AN AMALGAM** is an alloy of two or more metals, one of which is mercury.

Few metals are employed in the pure state, with the exception of iron, copper, lead, tin, zinc, platinum and aluminum; they are more frequently used for technical purposes in the form of alloys. Every industrial application requires special qualities that may not exist in any single metal, but which may be produced by the proper mixture of two or more. For example: silver and gold are much too soft and pliable for plate, coin or jewelry, but by the addition of certain amounts of copper they are rendered harder and more elastic, while their color and other valuable qualities are not impaired. Copper is also too soft and tough to be wrought in a lathe, but when alloyed with zinc, it forms a hard, beautiful, yellow-colored alloy known as brass, of great usefulness, and more easily worked than the pure metal.

Alloys are equally interesting, from a scientific standpoint, for they may be regarded not only as mere mixtures of metals, but in many instances as true chemical compounds. Matthiessen* regarded it as probable that the condition of an alloy of two metals in a melted state

*British Association Reports, 1863, p. 97.

may be either that of: (1) *A solution of one metal in another;* (2) *a chemical combination;* (3) *a mechanical mixture;* or, (4) *a solution or mixture of two or all of the above;* and that similar differences may exist as to its condition in the solid state, defining a solid solution as "a perfectly homogeneous diffusion of one body in another."

1. **A Solution of One Metal in Another.**—Some metals when melted together will apparently unite in the same manner that water mixes with alcohol, in all proportions and indefinitely, forming a perfect homogeneous mass and exhibiting no tendency to separate on cooling. The mixture thus formed will, as regards chemical and physical properties, be a mean of the two components; that is to say, it will partake of the properties of both, those of the one predominating just as one or the other may be in excess. Lead and tin form such an alloy.

2. **A Chemical Combination.**—Other metals when melted together do, without doubt, form true chemical compounds. In the phenomena which accompany such union, and in the properties of the resulting products, we observe that which characterizes the manifestation of affinity, that is, an *evolution of heat and light,* resulting in the formation of substances having a definite composition, *distinct crystalline form,* and a variety of properties different from those of the constituents. Thus, if a piece of clean sodium be rubbed in a mortar with a quantity of dry mercury, the sodium combines with a hissing sound, and a considerable increase of mass temperature is noticeable on the addition of each successive piece of sodium.

**EXPERIMENT No. 12.**—Throw a small piece of clean, dry sodium, upon the surface of a small amount of clean, dry, and warmed mercury; a chemical union takes place immediately, accompanied by **heat** and **incandescence**, forming crystalline amalgam.

When the mass cools, long needles of a white, brilliant alloy of definite composition crystallize from the middle of the liquid, and the excess of mercury may be separated by decantation. Platinum, iridium, gold, and silver unite with tin, accompanied by an evolution of heat. If the tin is in excess, upon cooling, the mass very much resembles that metal, but if the ingot be treated with strong hydrochloric acid, the excess of tin is dissolved, and crystals of a definite alloy of tin and the precious metals remain.* Examples of such union by definite proportion often occur in nature, as, for instance, we have the native alloys of gold and silver, in which four, five, six or twelve atoms of gold are found combined with one of silver. Several other metals, such as iridium and osmium, as iridosmine, palladium, and platinum and others occur as native alloys.

3. **A Mechanical Mixture.**—It must be admitted that in the case of mixing substances, or of dissolving one in another, the result is much dependent upon the affinity—or compatibility—existing between them. Thus we may attempt to dissolve camphor in water, but here the affinity is so feeble that an exceedingly small proportion will be dissolved; while, on the other hand, if we employ alcohol instead of water, a large quantity of the solid camphor may be taken into solution. Then, if water be subsequently added to such a solution, the spirit, having a greater affinity for the water than for the camphor, will leave the latter, to be separated again

*See chapter on Tin.

and assume a solid form. Thus, silver or gold will not unite with iron, nor zinc to any great extent with lead. Other metals melted together which possess little or no affinity for each other, do not readily unite, but remain separate and distinct; alloys of lead and copper, "pot-metal alloys," show on their fracture surfaces, when viewed under a strong glass, a network of copper and a small amount of lead, enclosing irregularly globular masses of nearly pure lead in its meshes. Such alloys are subject to liquation, or separation, by heat—the lead separating out, leaving the copper in a porous mass.

4. **A Solution or Mixture of Two or All of the Above.**—It is obvious that most alloys may be correctly classed under this head, when we consider the almost infinite proportions in which metals are combined.

**THE PHYSICAL PROPERTIES OF ALLOYS** can not be anticipated, and are only determinable by actual experiment. Very minute proportions of some metals added to others will produce an alloy with properties foreign to either of the constituents. Thus, a small quantity of lead fused with gold will produce a brittle alloy, though each metal is malleable.

**Specific Gravity.**—If this property be calculated from that of the components—assuming that there is no condensation of volume—the resulting number may be greater than, equal to, or less than, the experimental result. Thus, the alloys of silver and gold have a less specific gravity than the theoretical mean of the components; whereas copper and zinc vary in the opposite direction.

The following table,* by Thènard, shows examples of this variation:

| Alloys Possessing a Greater Specific Gravity than the Mean of Their Components | | | Alloys Having a Specific Gravity Inferior to the Mean of Their Components | | |
|---|---|---|---|---|---|
| Gold | and | Zinc | Gold | and | Silver |
| " | " | Tin | " | " | Iron |
| " | " | Bismuth | " | " | Lead |
| " | " | Antimony | " | " | Copper |
| " | " | Cobalt | " | " | Iridium |
| Silver | " | Zinc | " | " | Nickel |
| " | " | Lead | Silver | " | Copper |
| " | " | Tin | Copper | " | Lead |
| " | " | Bismuth | Iron | " | Bismuth |
| " | " | Antimony | " | " | Antimony |
| Copper | " | Zinc | " | " | Lead |
| " | " | Tin | Tin | " | Lead |
| " | " | Palladium | " | " | Palladium |
| " | " | Bismuth | " | " | Antimony |
| " | " | Antimony | Nickel | " | Arsenic |
| Lead | " | Bismuth | Zinc | " | Antimony |
| " | " | Antimony | | | |
| Platinum | " | Molybdenum | | | |
| Palladium | " | Bismuth | | | |

It is common among authorities who publish determinations upon specific gravities of the alloys to give the calculated as well as the observed specific gravity.

**The color** of an alloy usually resembles that of the metal which predominates. Some few exceptions are quite notable, for instance gold 2 to 6, and silver 1 part produces an alloy of a greenish color, and it is said that 1/24 part of silver is sufficient to modify the color of gold. Nickel and copper form alloys varying from copper-red to the bluish-white of nickel. With a content of 30 per cent of nickel the alloy is silver white; while with zinc, copper yields a variety of shades, from the silver white of brass consisting of copper 43, and zinc 57 parts, to that of red brass, which contains 80 per cent or more of copper.

*Phillip's Metallurgy.

**Malleability, Ductility, and Tenacity.**—These properties are generally very much modified by alloying. As a rule the malleability and ductility are decreased, even when two malleable and ductile metals, such as gold and lead, are alloyed together—a very small content of lead destroying the malleability and ductility of the noble metal. Again, copper 94 and tin 6 parts form an exceedingly brittle alloy. Generally the ductility decreases, while the hardness, as compared with that of the constituent metals, increases to a considerable extent, for example, gold and platinum, two very ductile and soft metals, afford an alloy much harder and of greater elasticity than either. Gold and silver, being too soft for currency, are alloyed with 10 per cent of copper, which gives them the required hardness. A few metals, antimony, for instance, possess the property of making metals harder. Mr. Makins states that 1-1900th part of this brittle metal will make gold quite unworkable. As a rule, a brittle and a ductile metal afford a brittle alloy; yet copper and zinc yield a malleable and ductile brass.

The tenacity is generally very much increased, as is shown by the following results of Matthiessen's experiments. Wires of the same gauge were employed, and the weights causing their rupture before and after alloying noted as follows:

| | Lbs. at Rupture |
|---|---|
| Copper, unalloyed | 25 to 30 |
| Tin, " | under 7 |
| Lead " | " 7 |
| Gold, " | 20 to 25 |
| Silver, " | 45 to 50 |
| Platinum, " | 45 to 50 |
| Iron, " | 80 to 90 |

| | Lbs. at Rupture |
|---|---|
| Copper, alloyed with 12 per cent Tin | 80 to 90 |
| Tin, " " " Copper | 7 |
| Lead, " " Tin | 7 |
| Gold, " " Copper | 70 |
| Silver, " " Platinum | 75 to 80 |
| Steel (iron compounded with carbon) | above 200 |

**Fusibility.**—The fusing point of an alloy is always lower than the least fusible metal entering into its composition, and is sometimes lower than that of any of the components. Thus an alloy composed of 10 parts lead and 4 parts tin fuses at 243° C., melting lower than the less fusible lead (327° C.), but at a greater temperature than tin (232° C.); and an alloy composed of 25 parts lead, 12.5 parts tin, 50 parts bismuth, and 12.5 parts cadmium (Wood's metal) melts at 65.5° C., lower than that of any of its constituents—tin being the most fusible (232° C.). Alloys of lead and silver, containing a small quantity of the latter, are more fusible than lead, and sodium and potassium form an alloy fluid at ordinary temperatures.

Matthiessen* explains why the fusing point of alloys is uniformly lower than the mean of those of their constituents: "It is generally admitted that matter in the solid state exhibits excess of attraction over repulsion, while in the liquid state these forces are balanced, and in the gaseous state repulsion predominates over attraction. Let us assume that similar particles of matter attract each other more powerfully than dissimilar ones; it will then follow that the attraction subsisting between the particles of a mixture will be sooner overcome by repulsion than will the attraction in the case

*Makins' Metallurgy, p. 65.

of a homogeneous body; hence, mixtures should fuse more readily than their constituents."

**Sonorousness.**—This property is most wonderfully developed in some instances. Copper and tin, two metals which possess the quality in but a small degree comparatively, unite to form an alloy known as "bell metal," the normal composition of which is, copper 74 or 85, and tin 26 or 15, respectively. Copper and aluminum also yield alloys of remarkable sonorousness.

**Conductivity.**—The property of conductivity, either for electricity or heat, in an alloy is much inferior to that of the pure metals. Advantage is taken of the high electrical resistance in some of the alloys, such as German silver, for measuring the resistance of long lines of telegraph wire, the electromotive force or working power of batteries, for making rheostats and other apparatus for controlling the electric current, etc.

**Decomposition.**—Heat decomposes alloys containing volatile metals like mercury or zinc. It requires a temperature much above the boiling point of the metal, however, to completely separate all traces of it from an alloy, and in most instances this can not be accomplished even then without the assistance of a chemical agency. When gold is contaminated with tin, the latter can not be removed entirely by roasting; but if heated with small quantities of potassium nitrate, which serves to oxidize the base metal, it may be entirely removed. Mercury may be completely separated by roasting; it volatilizes at about 357.3° C. When endeavoring to expel it from old amalgam fillings, however, the plug should be heated bright red.

**ANNEALING AND TEMPERING.**—Annealing is a process employed in the working of various metals and

alloys to reduce the brittleness and stiffness usually resulting from a rapid or important change of molecular structure, such as is produced by hammering, long continued vibration, rolling, and sudden cooling. Bell metal is brittle, and cracks under the hammer, cold as well as heated. If it be repeatedly brought to a dark-red heat and quickly cooled by immersion in water, its brittleness is so far decreased that it can be hammered and stamped.

The dentist, in swaging a flat sheet of gold alloy to conform to his dies, must stop at intervals and anneal the piece of metal to prevent its splitting under his blows and pressure.

It is said sudden changes of temperature have the effect, almost invariably, of rendering metals brittle. *Gold, silver, platinum,* etc., should be heated for a rearrangement of their molecular structure and allowed to slowly cool, rather than to be immediately plunged into a cold bath, if the best results are desired. *Lead, tin,* and *zinc* are annealed by immersion in water, which is made to boil and then cool slowly. *Steel* should not be annealed in an *open* fire, as the carbon which enters the iron as an element, combines with the oxygen of the air to the detriment of the steel.

Annealing may be said to be the inverse process of—

**Tempering,** which latter is the fixing of the molecular condition of steel by more or less sudden cooling from a particular temperature.

**Oxidation.**—Alloys are usually more easily oxidized than their constituents.

Nearly all metals in a state of fusion have a tendency to dissolve a greater or less amount of their oxides, and this is particularly true of alloys, for then the metals

are in a state of solution, a condition most favorable to chemical change.

The best preventive against this formation of oxides and their subsequent absorption is to protect the molten alloy by a layer of pulverized charcoal or some of the fluxes. A reduction of much of the oxide formed may be effected by vigorous stirring with a stick of green wood. The careful addition of not more than 0.008 to 0.0010 parts of phosphorous has been found an excellent agent for the deoxidation of the oxides dissolved in bronze.

The zinc and alloys used in the dental laboratory for making dies, after repeated melting and casting in contact with the air, often become thick and mushy from dissolved oxides; and their valuable working qualities are so seriously impaired that they fail to copy the fine lines of the mold and produce a perfect die. Their properties may be restored to a great extent by melting under pulverized charcoal or tallow, and vigorously stirring with a stick of green wood, or by dissolving in the molten metal a small quantity of aluminum.

**INFLUENCE OF CERTAIN METALS IN ALLOYS.**—Certain metals when present in an alloy confer upon it definite properties which are in many instances characteristic; thus, in a general way, mercury, cadmium, and bismuth increase fusibility; tin, hardness and tenacity; antimony and arsenic, hardness and brittleness.

**A SOLDER** is an alloy or metal used for cementing or binding metallic surfaces or margins together, and

the process is usually effected by heat. Ordinary solders are divided into hard and soft classes.

*The Hard Solders* comprising those which require a red heat for their melting.

*The Soft Solders* being those used by plumbers and tinsmiths, and consisting principally of lead and tin, with sometimes an addition of bismuth.

*Brazier's Solder,* for uniting the surfaces of copper, brass, etc., is usually composed of copper and zinc, nearly equal parts, with a small addition of tin, and sometimes antimony.

Silver is the proper solder for German silver articles, and gold or an alloy of gold and platinum for platinum.

**In Soldering,** the surfaces or edges to be united must be kept free from oxidation and dirt. To keep them deoxidized during the operation several fluxes are used, such as dehydrated borax, or some of the reliable prepared compounds on the market, for gold, silver, brass, or copper soldering; rosin, or a solution of zinc chloride, for tin plate; zinc chloride for zinc, hydrochloric acid for galvanized iron, and rosin and tallow for lead and tin.

Burnley's soft soldering paste consists of 2 oz. of a saturated solution of zinc chloride mixed with one pound of petrolatum or vaseline. It is most convenient when placed in a container like a tooth paste tube with a long aluminum nozzle.

Among the requirements of a good gold solder the most important are *carat, color, strength,* and *fusing point.* In fineness it should be equal, or nearly equal, to the plate, its color and strength as nearly as possible the same, while the fusing point should be a trifle

lower—the nearer the melting point of the plate the better the results.

To obtain these qualities it is necessary to prepare a solder by the addition of some metal which will fuse at a lower temperature than any of the constituents of the plate. Zinc is admirably suited for this purpose, and is generally used, since it permits of a solder as fine, or nearly as fine as the plate. In addition to this it also possesses the advantage of yielding a less fluid solder than that of copper and silver, permitting it to bridge over slight spaces. This is very probably on account of the oxidation or volatilization which takes place, for it is observable that any subsequent fusing requires a greater heat. An advantage is also obtained here in this fact, since it enables more perfect second solderings with the same alloy.

The process of soldering is a cementation by superficial alloying, and is admirably illustrated in the instance of soldering platinum bases with pure gold for continuous-gum dentures. By means of the blow pipe the gold is flowed over the surfaces of platinum, joining them, but if the joint is not well made, and the intervening space is filled with gold, it is not as strong as it might be. This, however, is all remedied during the process of baking the body and enamel, as the high heat required for this so diminishes the cohesive power of the platinum that it readily and completely alloys with the gold, producing a stronger joint of a platinum-gold alloy, which is observed to be the same color as the platinum.

Soldering iron or steel, except galvanized iron, is more difficult than any of the soldering operations, aluminum excepted. It is due to surface oxidation and

lack of affinity. Before soldering iron, it is necessary to tin it when soft solder is used. This is like a plating process. The surface must be free from oxides. This may be accomplished by first immersing in benzine, or potassium hydroxide or lye solutions until the grease is removed, then placed in a 10 per cent solution of sulphuric acid until the oxide is removed, and finally immersing in strong solution of sodium hydroxide. The iron may now be coated with a light coat of copper by immersing in a copper sulphate solution, after which it may be tinned by heat in the usual manner or it may be tinned without first depositing copper. The former method gives a more adhesive coat of tin and lead.

**Autogenous Soldering** is a process of uniting by direct fusion of the contiguous parts, without the intervention of a more fusible alloy. It is extensively used in uniting ends of bands for collar crowns.

**PREPARATION OF ALLOYS.**—This would seem but a simple task, but in order to produce an accurate result it is far from being as easy as it may seem. Most alloys are prepared by directly melting the metals together, but much skill, judgment, and experience are required to determine when it is best to add each constituent, and the amount of each to be used—to protect the molten mass, and to handle it generally.

The metal having the highest fusing point is generally melted first, and the others are added in accordance with their points of fusibility. To obtain as homogeneous an alloy as possible, the metals, while in a state of fusion, must not be allowed to remain quiescent, but an intimate mixture effected by vigorous stirring, sticks of dry soft wood being used for the purpose. By stir-

ring the fused mass with one of these sticks, the wood is more or less carbonized according to the temperature of the mass, gases are evolved from the carbonizing wood, which, by ascending in the fused mass, contribute to its intimate mixture. The stirring should continue for some time and the alloy then cooled as rapidly as possible.

The varying densities of the metals to be combined frequently render the formation of a homogeneous mass very difficult. In some instances the heavier metal tends to sink to the bottom, carrying with it a small quantity of the other, while the lighter, floating above, retains a small quantity of the heavier. For instance, only a small proportion of zinc will unite with lead, or aluminum with bismuth; but, as a rule, metals mix perfectly in the fluid state. When, however, the fluid mixture is poured into the ingot mold, it rarely happens that the solidified mass is perfectly homogeneous. The reason of this is that the addition of one metal to another produces an alloy, the solidifying point of which is usually lower than it should be according to calculations based upon the proportionate amounts and fusing points of the constituents. One particular mixture has a lower fusing point than any other possible mixture of the metals employed, and this is termed the eutectic alloy of that series. Aside from those possibly true chemical combinations of metals, a fluid mixture of two metals may be expected to begin depositing its less fusible constituent first, and, as the temperature falls, more and more of this element will be separated, the other constituent concentrating in the fluid residue until this has acquired the eutectic composition, when it will solidify as a whole in the spaces

left between the already solidified particles. The more slowly the material solidifies, the more marked will be the separation that occurs.

**EUTECTIC ALLOYS.**—In 1884 the late Professor Guthrie introduced the term **eutectic** to denote the most fusible alloy of two or more metals. He compared it to the mother liquor of a salt solution, which remains fluid after the bulk of the salt has separated out. At a temperature near the melting point of lead a mixture of equal parts of Pb and Sn would be fluid. If the alloy were cooled down to 220° C., the lead would crystallize out, and a solid lead would exist in contact with liquid lead. As the mixture cooled, more and more lead would crystallize out until at 180° C. the whole would solidify. The residue would now consist of about 70% tin and 30% lead. This, therefore, is the eutectic alloy. The reverse would happen if there was more tin than lead in the alloy; then the tin would separate out. The minute structure of the cold alloy would appear as a mass of lead crystals in the eutectic of lead and tin.

Eutectics are not always as simple as this, for if there is more than one solution and each solution on cooling will give a deposit and a eutectic, the eutectic is not a chemical compound, for it is never in molecular proportions.

Authorities differ on this point, as Flavitzkii (Phys. Chem. Soc. 42,428-34) considers cryohydrates and eutectics to be definite chemical compounds. Conversely, many chemical compounds might be regarded as eutectics. If the determination of eutectics depends entirely on the lowest fusing point of alloys of certain metals in definite chemical proportions, then the results of some

experiments would tend to disprove Flavitzkii's statement. (See following table.)

| Lead | Tin | Bismuth | Cadmium | Fusing point, C. |
|---|---|---|---|---|
| 25.00 | 12.50 | 50.00 | 12.50 | 55.5 |
| 12.00 | 216.00 | 60.00 | 12.00 | 55.5 |
| 34.97 | 9.90 | 35.13 | | 90. |
| 31.25 | 18.75 | 50.00 | | 90. |
| 16.67 | 41.67 | 41.66 | | 100. |
| 25.00 | 25.00 | 50.00 | | 100. |

For making large quantities of an alloy the reverberatory furnace is used, special precautions being taken to preserve a deoxidizing flame within the furnace.

For preparing alloys in a small way a crucible is used, and the alloy is covered with a suitable flux to protect it from the action of atmospheric air. Four sources of loss must be guarded against: (1) loss by oxidation; (2) loss by volatilization; (3) loss by chemical combination with the flux; (4) loss by fracture or solution of the crucible.

The first may be prevented by the use of one of the various fluxes,* or covering the surface with pulverized charcoal. The second loss usually occurs through an endeavor to alloy a metal of a high fusing point with one which fuses at a low temperature. Under such circumstances the one requiring a high temperature should be fused first and well covered with flux melted to extreme fluidity; the more fusible metal should then be added in as large a piece as convenient and quickly thrust beneath the molten surface. The third source of loss is principally caused by the use of borax as a flux for some base metals. It is well known that in much borax a portion of the boric acid is not perfectly

*See chapter on Melting Metals.

saturated, and this is especially true of the prepared article; and if melted with some base metals, the free acid is absorbed, which, with the sodium borate, forms double salts of a glassy nature. Hence, by fusing some metals and alloys under borax, a certain portion will be lost in chemical combination. The fourth cause is guarded against by careful selection of crucibles. If alloys of low fusing metals are to be made, the ordinary clay or Hessian crucible is all that is necessary, and, indeed, with proper care, noble metals may be alloyed in it without danger of loss; but it is liable to perforation by corrosive fluxes, allowing the molten alloy to escape. Therefore, for the preparation of expensive alloys from noble metals, the employment of tried graphite or graphite and clay crucibles often saves much trouble and expense.

In some instances, especially when metals are known to form chemical combinations, it may be best to melt the one of lowest fusing point first, and then dissolve the other components in it. Or, those of low fusing point may be melted in one crucible, while those more difficult of fusion are melted in another, then combined in the molten state.

When two metals of varying specific gravity are alloyed, the mass should not be allowed to become quiescent just before pouring. And if any incompatibility exists between the metals, such as in the case of zinc and lead, accompanied by a great difference in specific gravity, an intimate admixture should be effected by vigorously stirring the molten mass with sticks of soft, dry wood, which become more or less carbonized, according to the temperature of the mixture. In consequence of this dry distillation of the

wood there is evolved an abundance of gases, which by ascending in the fused mass, contribute to its intimate mixture. The stirring should be continued for some little time, and the alloy poured as quickly as possible.

"Many alloys," says Mr. Brannt,* "possess the property of changing their nature by repeated remelting, several alloys being formed in this case, which show considerable differences, physically as well as chemically. The melting points of the new alloys are generally higher than those of the original alloy, and their hardness and ductility are also changed to a considerable extent. This phenomenon is frequently connected with many evils for the further application of the alloys, and in preparing alloys showing this property the fusion of the metals and subsequent cooling of the fused mass should be effected as rapidly as possible."

Although most of the heavier metals are at present used in the preparation of alloys, copper, zinc, tin, lead, silver, and gold are more frequently employed than all others. Alloys containing nickel have become of great importance, as well as those in which aluminum forms a constituent.

Mr. Brannt recommends for experimentation that metals be added to each other in certain quantities by weight, which are termed atomic weights, and claims that in this manner alloys of determined, characteristic properties are, as a rule, produced; or, if such does not answer the demands of the alloy, the object may be attained by taking two, three or more equivalents of the metal, exception being made in the cases of arsenic and such elements.

*Metallic Alloys, p. 87.

# CHAPTER VI

## LEAD

| | |
|---|---|
| Plumbum. | Symbol, Pb. |
| Valence, II, IV. | Specific gravity, 11.34. |
| Atomic weight, 207.2. | Malleability, 7th rank. |
| Melting Point, 327° C. | Tenacity, lowest (8th) rank. |
| Ductility, 10th rank. | Chief ore, galenite. |
| Conductivity (heat), 8.36. | Conductivity (electricity), 8.4. |
| (Silver being 100.) | |
| Specific heat, 0.0310. | Crystals, octahedral. |
| Color, bluish-white. | |

**OCCURRENCE.**—This abundant and very useful metal is almost wholly obtained from its native sulphide, (1) *Galenite* (PbS) or galena, and is rarely, if ever, found free. Its other more widely distributed ores are (2) *Cerusite* ($PbCO_3$), lead carbonate, sometimes called white-lead ore, and (3) *Crocoisite* ($PbCrO_4$), lead chromate. There is also a (4) *Wulfenite* ($MoO_4Pb$) and a (5) *Sulphate* ($PbSO_4$). Galenite often carries silver, as AgS, in sufficient quantities to be well worth extracting, the proportion of the noble metal varying from about 0.01 to 0.03 per cent, and in rare cases amounting to 0.5 or 1 per cent. Such ore is called *Argentiferous Galena.* Lead ore frequently occurs accompanied by copper, iron pyrites, and zinc-blende. Galenite is found in the United States, Great Britain, Spain and Saxony.

**REDUCTION OF GALENITE** is effected in a reverberatory furnace, into which the crushed lead ore is

introduced and roasted for some time at a dull-red heat. In the roasting a portion of the lead sulphide is oxidized to the oxide and sulphate—

$$PbS + 3O = PbO + SO_2 \text{ and}$$
$$PbS + O_4 = PbSO_4.$$

The contents of the furnace are then thoroughly mixed and the temperature raised, whereupon the sulphate and oxide react with the remaining sulphide, forming sulphurous oxide and metallic lead—

$$2PbO + PbS = SO_2 + 3Pb \text{ and}$$
$$PbSO_4 + PbS = 2SO_2 + 2Pb.$$

Contaminating metals, which render the lead hard, are removed by melting and partially oxidizing in a reverberatory furnace with a cast-iron bottom.

**PROPERTIES.**—Pure lead is a feebly lustrous, bluish-white metal, endowed with a high degree of softness and plasticity and almost entirely devoid of elasticity. It is said to be the least tenacious of all metals in common use. A wire 0.1 inch in thickness is ruptured by a weight of about thirty pounds. Its specific gravity is 11.34. It melts at 327° C. At a bright-red heat it vaporizes, and at a white heat (1580° C.) it boils. Its specific heat is .0310, that of water at 0° C. being taken as a unit. Lead exposed to ordinary air is rapidly tarnished, forming a **suboxide.** The same supposed suboxide is formed upon lead kept in a state of fusion in the presence of air, when at the same time the metal rapidly absorbs oxygen; then the monoxide (PbO) is formed, the rate of oxidation increasing with the temperature. By slowly cooling lead may be ob-

tained in octahedral crystals. Dilute acids, with the exception of nitric, act but slowly on lead.

**DENTAL APPLICATIONS.**—Its chief dental use is in the laboratory as a counterdie. It may be rolled into a thin foil, and at one time was used for filling carious teeth, and in conical points was used in filling the apices of pulp-canals. It is an important component of soft solders and various alloys.

**COMPOUNDS WITH OXYGEN.**—There are four compounds of lead and oxygen:

The **Diplumbic Oxide,** or *Lead Suboxide,* $Pb_2O$, a gray pulverulent substance, is formed when the monoxide is heated to a dull redness in a retort, and is supposed to correspond with the dull coating formed on bright, freshly cut surfaces of lead when left exposed to the air.

The **Monoxide,** *Litharge* or *Massicot,* PbO, is very heavy, and of a delicate straw-yellow color, slightly soluble in water, melting at a red heat, with a tendency to crystallize on cooling, and is easily reduced when heated with organic substances of any kind containing carbon or hydrogen. It is the product of the direct oxidation of the metal, but is more conveniently prepared by heating the carbonate to dull redness.

$$PbCO_3(+\text{heat}) = PbO + CO_2.$$

The **Dioxide,** *Puce* or *Brown Lead Oxide,* $PbO_2$, is a heavy brown powder, insoluble in water, having an acid reaction, and may be regarded as the anhydride of plumbic acid, $H_4PbO_4$. It is easily obtained by digesting the red oxide in nitric acid.

**Red Oxide,** or *Red Lead,* is a compound of the mon- and dioxides, not very constant in its composition, but

is generally regarded as having the formula 2PbO, $PbO_2 = (Pb_3O_4)$. It is a heavy, bright-red powder, and may be regarded as lead plumbate, $Pb_2PbO_4$. It is used as a cheap substitute for vermilion. When treated with dilute nitric acid the monoxide dissolves, forming soluble lead nitrate, leaving the puce-colored oxide behind. It is prepared by exposing the monoxide, which has not been fused, for a long time to the air at a very faint red heat.

**ACTION OF ACIDS ON LEAD.**—The presence of carbonic acid in a water does not affect its action on lead. Aqueous nonoxidizing acids generally have little or no action on lead in the absence of air.

**Sulphuric Acid,** when dilute (20 per cent solution or less), has no action on lead, even when air is present, nor on boiling. The stronger acid does act, slowly in general, but appreciably, the more so the greater its concentration and the higher its temperature. Pure lead is more readily acted upon than that contaminated with antimony or copper. Boiling concentrated sulphuric acid converts lead into the sulphate, with the indirect evolution of sulphurous oxide.

$$Pb + H_2SO_4 = PbSO_4 + 2H$$
$$2H + H_2SO_4 = 2H_2O + SO_2$$

Nascent hydrogen reacts with sulphuric acid to produce $SO_2$. If there is sufficient hydrogen it will reduce $H_2SO_4$ to $H_2O + S$.

**Nitric Acid.**—The metal is readily dissolved in dilute nitric acid, nitrogen dioxide being evolved and plumbic nitrate formed.

**Hydrochloric Acid.**—Strong and hot hydrochloric

acts but slowly upon lead, forming the dichloride and liberating hydrogen.

**Water,** when pure, has no action on lead *per se.* In the presence of free oxygen (air), however, the lead is quickly attacked, forming a hydrated oxide, Pb2HO or $PbOH_2O$, which is appreciably soluble in water, rendering the liquid alkaline. When carbonic acid is present the dissolved oxide is soon precipitated as basic carbonate—$PbCO_3$ (which is slightly soluble in water containing carbon dioxide)—so there is room made, so to say, for fresh hydrated oxide, and the corrosion of lead progresses. Now, all soluble lead compounds are strongly cumulative poisons; hence the danger involved in using lead pipes or cisterns in the distribution of PURE waters. We emphasize the word "pure," because experience shows that the presence in water of even small proportions of bicarbonate or sulphate of lime prevents its action on lead. These sulphates or carbonates almost invariably present, cause the deposition of a very thin but closely adherent film of sulphates or carbonates upon the surface of the metal, which protects it from further dissolution.

**ALLOYS.**—Pure lead unites with almost all metals. Mercury readily amalgamates with it, and, in proper proportions, crystallizes, forming a very white but brittle alloy. This union is said to be of a definite chemical proportion, and is expressed as $Pb_2Hg$. Very small quantities of lead admixed with the noble metals destroy completely their malleability, and hence renders them unworkable. It is said that 1-1920th part of lead in *gold* will greatly impair its coining property, and that gold containing 1-500th part of lead is "rendered unfit for coinage." The gold drawer in the

dental laboratory is often so situated that it is almost impossible to prevent particles of lead from accumulating with the gold scraps and filings. These, however, may be easily removed by roasting with potassium nitrate and sulphur.*

**Silver** in certain proportions with lead forms an alloy which has a lower fusing point than that of lead. Pattinson, taking advantage of this fact, invented his process for recovering the silver from argentiferous galena. A quantity of the silver-lead ore is melted in one of a series of iron pots. After complete fusion it is allowed to slowly cool, when the poorer lead crystallizes and is ladled off to another pot, leaving the rich silver-bearing lead behind. This is carried on through the whole series of some twelve pots, until the lead-silver alloy has been reduced to proportions by which the noble metal may be recovered by the process of cupellation.†

**Platinum** with equal weight of lead gives a purplish-white, brittle, and granular alloy. So great is the affinity these metals have for each other that lead oxide heated in a platinum crucible with reducing flux is broken up and the lead combines with the platinum vessel. Lead can only be separated from platinum by the humid process of refining platinum.

**Palladium** and lead form a green alloy which is very hard and brittle.

The more common alloys of lead are those with tin, antimony, etc.

**Tin** unites with lead in almost any proportion with slight expansion.‡

*See chapter on Gold.
†See chapter on Silver.
‡Kuppfer.

The following table gives an idea of the melting points of alloys of lead and tin:

| An Alloy of— | Fuses at— |
|---|---|
| Lead 1, Tin 2 | 171.° C. |
| " 1, " 6 | 194.4° C. |
| " 2, " 1 | 227.7° C. |
| " 4, " 1 | 259.° C. |
| " 17, " 1 | 289.° C. |

With tin 1 part and lead 5 parts* Dr. Haskell makes counterdies to be used with his Babbitt-metal dies. It fuses at a lower temperature than the die alloy, and also has the advantage of being harder than lead, which he claims is too soft for counterdies. Tin-lead alloys are used largely in soldering.

The following are compositions and melting points of frequently used compounds:†

| Grade | Tin | Lead | Melts at— |
|---|---|---|---|
| Fine Solder | 2 | 1 | 171.° C. |
| Common " | 1 | 1 | 188.° C. |
| Coarse " | 1 | 2 | 227.7° C. |

Pewter may be said to be substantially an alloy of the same two metals; but small quantities of copper, antimony, and zinc are frequently added. Common pewter contains about 5 parts of tin for 1 of lead. In France a tin-lead alloy, containing not over 18 per cent of lead, is recognized by law as being fit for measures for wine or vinegar. "Best pewter" is simply tin alloyed with a mere trifle (½ per cent or less) of copper.

**Antimony.**—Lead contaminated with small proportions of antimony is more highly proof against vitriol

*The author has found the fusing point of this alloy to be 192.2° C.
†Tomlinson.

than the pure metal. An alloy of 83 parts of lead and 17 parts of antimony is used as type metal; other proportions are used, however, and other metals added besides antimony (e. g., tin, bismuth) to give the alloy certain properties.

**Arsenic** renders lead harder. An alloy made by the addition of about 1/56 of arsenic is used for making shot.

Lead forms a very important part in "fusible alloys."*

**TESTS FOR LEAD IN SOLUTION.**—In testing various solutions, first pour about three c.c. of the solution to be tested in a test tube, and add a few drops of the selected reagent. Sometimes the precipitate is soluble in an excess of this reagent, and sometimes in excess of either solution or reagent. If there be reason to suspect either, proceed cautiously, adding but a drop at a time, until a sufficient precipitate has been thrown down. If the first few drops of the reagent added cause a precipitate which is immediately redissolved, it shows that it is soluble in an excess of the solution, and if it be also soluble in an excess of the reagent, an equilibrium must be attained. After the precipitate has thoroughly settled, note its color and general appearance; then decant the supernatant liquid as thoroughly and carefully as possible, and divide the precipitate in as many other test tubes as may be desired for testing its solubility in the various reagents.

**Sulphuretted hydrogen** is one of the most important reagents used in tests for salts of metals in solution. To the suspected solution add, drop by drop, the saturated solution of sulphuretted hydrogen ($H_2S$); a black

*See chapter on Bismuth.

precipitate is quickly formed, which is insoluble in an excess of the reagent. To the suspected solution add a few drops of *ammonium hydrosulphide,* $(H_4N)HS$; a black precipitate, insoluble in an excess of the reagent, is formed.

**Potassium hydrate or ammonia** throws down a white precipitate—hydrated oxide. This is soluble in an excess of the potassa, but not of the ammonia.

**Alkaline carbonates** precipitate the white plumbic carbonate, which is quickly blackened by sulphuretted hydrogen.

**Sulphuric acid** is a characteristic test, precipitating a white sulphate.

**Hydrochloric acid** or a chloride gives a white precipitate soluble in an excess of potassa.

**BLOWPIPE ANALYSIS.**—A lead-salt is easily reduced on a piece of charcoal before the blowpipe, a bead of lead ultimately resulting in the center of the point of fusion, around which the charcoal will be seen to have absorbed a portion of the yellow monoxide of lead. The bead may be readily recognized as metallic lead, which is soft and may be readily flattened or cut with a knife. "If the lead contains silver, the latter is easily detected by the use of bone-ash. Fill a bowl-shaped cavity in the charcoal with finely powdered bone-ash, pressed down well, so as to fill the cavity with a compact mass, smooth, and slightly hollowed on the surface. In this, place a small quantity of the lead, hold the charcoal horizontally, and direct the extreme point of the *outer* (oxidizing) flame upon the metal. The bone-ash will absorb the lead oxide formed, leaving a metallic globule of silver. The latter may be covered with a thin film of oxide, showing rainbow tints. When the color ceases, and the globule no longer dimin-

ishes in size, it is pure silver. The process is hindered by the presence of tin."*

On **charcoal** in either flame lead is reduced to a malleable metal, and yields near the assay a dark lemon-yellow coat, sulphur-yellow when cold, and bluish-white at border.

With **bismuth flux: On plaster,** a chrome-yellow coat, blackened by ammonium sulphate.

**Interfering Elements.—Antimony.**—Treat on coal with boracic acid, and treat the resulting slag on plaster with borax flux.

**Arsenic Sulphide.**—Remove by gentle oxidizing flame.

**Cadmium.**—Remove by reducing flame.

**Bismuth.**—Usually the bismuth flux test on plaster is sufficient. In addition the lead coat should color the reducing flame blue.

**ELECTRODEPOSITION OF LEAD.**—In a solution of hyponitrite, nitrate or acetate of lead, zinc receives a coating, or its place may be taken entirely by the lead.

**EXPERIMENT No. 20.**—Dissolve one gram of the nitrate or acetate of lead in about 500 c.c. of distilled water and put the solution in a bottle. Suspend a piece of granulated zinc or a spiral of zinc wire in the center of the solution and let it stand. The lead will be deposited slowly in a crystalline form, known as **arbor plumbi.** At the same time the zinc will pass into solution, the lead simply replacing the zinc. After the tree has been formed, filter off some of the solution and see whether or not zinc is contained in it. There will probably be some lead left. In order to detect the zinc, the lead will have to be removed. This may be done by adding sulphuric acid (forming the sulphate) and alcohol (to prevent its being redissolved). Filter off the lead sulphate, and to the filtrate add just enough **ammonia** to neutralize the **sulphuric acid,** and then test with **ammonium hydrosulphide;** white zinc sulphide is precipitated.

*Dr. Clifford Mitchell.

## CHAPTER VII

## ANTIMONY

| | |
|---|---|
| Stibium. | Symbol, Sb. |
| Valence, III, V. | Specific gravity, 6.62. |
| Atomic weight, 120.2. | Malleability, brittle. |
| Melting point, 630° C. | Tenacity, brittle. |
| Ductility, brittle. | Chief ore, stibnite. |
| Specific heat, 0.0495. | Crystal, rhombohedral. |
| Conductivity (heat), 3.6. | Conductivity(electricity), 4.42 |
| Color, bluish-white. | |

**OCCURRENCE.**—Antimony is found in the metallic state to a small extent in many of the localities from which its ores are derived. It occurs alloyed with other metals, such as silver, nickel, copper, and iron, and usually contaminated with arsenic. Commercial antimony is obtained almost entirely from its chief ore, *stibnite,* the sulphide, $Sb_2S_3$, which is found in great abundance in Borneo, New Brunswick, and Nevada. This ore usually occurs in veins, and has a leaden-gray color, with a metallic, sometimes iridescent, luster.

**REDUCTION.**—The metal is easily reduced by heating the ore in a furnace with about half its weight in scraps of metallic iron, whereupon it gives up its sulphur, which unites with the iron, forming ferrous sulphide, and liberates antimony.

$$Sb_2S_3 + 3Fe = Sb_2 + 3FeS.$$

The process is usually carried on in perforated tubes or kettles to allow the antimony to separate from the gangue.

The metal is so frequently contaminated with arsenic that it can not be safely used for dental purposes until it has gone through a refining process.

**PROPERTIES.**—Pure antimony is a brilliant, somewhat iridescent, bluish-white metal, readily crystallizing in rhombohedrons, which form large stellate figures on the fused surface when cooled. It fuses at 630° C., and may be distilled at a white heat in an atmosphere of hydrogen. When heated to redness it takes fire, burning with a brilliant white flame. It undergoes no change in air at ordinary temperatures, but is easily oxidized when heated to fusion. It is an important metal in the manufacture of alloys, increasing their hardness even when mixed in very small quantities, and Roberts-Austen states that it is one of the two metals which expand on solidification, the other being bismuth. The finely powdered metal takes fire spontaneously when thrown into chlorine gas, forming chlorides.

**COMPOUNDS WITH OXYGEN.**—Antimony forms *two* distinct oxides:

The **Trioxide,** or *Antimonous Oxide,* $Sb_2O_3$, occurs native, though rarely. It may be prepared by burning metallic antimony at the bottom of a large red-hot crucible. It is a pale buff-colored powder, fusible, volatile, of basic reaction, and having double molecules $(Sb_2O_3)_2$ like arsenic, it readily absorbs more oxygen changing to $Sb_2O_4$. When boiled with potassium bitartrate, it is dissolved, and the solution yields on evaporation crystals of *tartar emetic,* $KSbOC_4H_4O_6$.

The **Pentoxide,** or *Antimonic Oxide,* $Sb_2O_5$, is obtained by the action of strong nitric acid on antimony. It is a pale straw-colored powder, of acid reaction, insoluble

in water or acids, decomposes on being heated, passing to the intermediate oxide, $Sb_2O_3$,$Sb_2O_5$.

The **Intermediate Oxide**, or *Tetroxide*, $Sb_2O_4$, as it is sometimes called, $Sb_2O_3$, $Sb_2O_5$, is obtained by heating the pentoxide in the air, and is recognized as an infusible, nonvolatile and insoluble, grayish-white powder.

**ACTIONS OF ACIDS ON ANTIMONY.—Hydrochloric acid,** boiling and concentrated, *slowly* dissolves powdered antimony, forming antimonous chloride and liberating hydrogen—

$$Sb + 3HCl = SbCl_3 + 3H,$$

but when the metal is in the compact state, it resists this acid.

**Sulphuric acid,** boiling and concentrated, *slowly* converts it into antimonous sulphate with an evolution of sulphur dioxide—

$$2Sb + 6H_2SO_4 = Sb_23SO_4 + 6H_2O + 3SO_2.$$

**Nitric acid** rapidly oxidizes the metal, the dilute acid forming chiefly antimonous oxide—

$$2Sb + 2HNO_3 = Sb_2O_3 + H_2O + 2NO,$$

while the concentrated form yields some antimonic oxide

$$6Sb + 10HNO_3 = 3Sb_2O_5 + 5H_2O + 10NO.$$

For the most part the intermediate is the result of this action—

$$6Sb + 8HNO_3 = 3Sb_2O + 4H_2O + 8NO.$$

**Nitro-hydrochloric acid** converts it into soluble antimonous chloride and insoluble oxides, and is the only satisfactory solvent.

**Tartaric acid** in a boiling solution *slowly* dissolves precipitated antimony—

$$2Sb + H_2(C_4H_4O_6) + 2H_2O = (SbO)_2C_4H_4O_6 + 6H.$$

**Alkalies** do not dissolve it.

**ALLOYS.**—The metal is chiefly valuable for the alloys it yields with other metals, and, as has been said, possesses the quality of increasing the hardness of those alloys. Antimony also causes expansion in most alloys, if in excess of 22 parts per 100, thereby copying fine lines and sharp casts; hence, its great value in the manufacture of type. In many cases it renders the alloy very brittle, and is especially injurious to the noble metals or copper, destroying their malleability, ductility, etc.

**Mercury.**—The *amalgam* of antimony is soft and easily decomposed. Experiments have been made, with a view to using this element in dental-amalgam alloys, but to no profit.

**Gold.**—One grain of antimony to 2000 will greatly injure the malleability of gold.

**Copper** containing 1/1000 of this metal can no longer be worked for sheet-brass.

**Tin.**—Antimony is added to tin alloys to give hardness and expansion, but renders most of them very brittle.

**Bismuth** forms with antimony a grayish, brittle and lamellar alloy. In order to remove the brittleness varying quantities of tin are added, as is also lead, or both. The fusibility then rather increases, instead of decreasing.

*Some alloys containing antimony:*

**Cliché metal,** tin 48, lead 32.5, bismuth 9, and antimony 10.5.

**Babbitt metal,** copper 4, tin 12, and antimony 8, melted separately. The antimony is added to the tin, then the copper, and 12 parts more tin after fusion.

TYPE METAL—TABLE OF COMPOSITION*

| Metal | Parts | | | | |
|---|---|---|---|---|---|
| | I | II | III | IV | V |
| Lead | 3 | 10 | 70 | 6 | 100 |
| Antimony | 1 | 2 | 18 | ..... | 30 |
| Copper | ..... | ..... | 2 | 4 | 8 |
| Bismuth | ..... | 1 | ..... | ..... | 2 |
| Zinc | ..... | ..... | ..... | 90 | ..... |
| Tin | ..... | ..... | 10 | ..... | 20 |
| Nickel | ..... | ..... | ..... | ..... | 8 |

**Britannia Metal** (Wagner's).—Tin 85.64, antimony 9.66, copper 0.81, zinc 3.06, and bismuth 0.83.

**Queen's Metal.**—Tin 88.5, antimony 7.1, copper 3.5, and zinc 0.9.

**TESTS FOR ANTIMONY IN SOLUTION.—Sulphuretted Hydrogen** added to an *acidulated* solution of antimony occasions an immediate precipitate of very characteristic orange-red color.

**Potassa, or ammonia,** or their carbonates, throw down a bulky white hydrate, of which that formed by potassa is soluble in excess of alkali, but the hydrate formed by the ammonia or alkaline carbonates is nearly insoluble.

If a hydrochloric acid solution be treated with a quantity of water, an immediate precipitate of oxychloride falls, soluble in tartaric acid, distinguishing it from bismuth.

$$3SbCl_3 + 4H_2O = Sb_3O_4Cl + 8HCl.$$

*Table from Brannt.

## CHAPTER VIII

## TIN

| Stannum. | Symbol, Sn. |
|---|---|
| Valence, II, IV. | Specific gravity, 7.29. |
| Atomic weight, 118.7. | Malleability, 5th rank. |
| Melting point, 232° C. | Tenacity, 7th rank. |
| Ductility, 9th rank. | Chief ore, tinstone. |
| Conductivity (heat), 15.28. | Conductivity (electricity), 14.4. |
| (Silver being 100.) | |
| Specific heat, 0.0559. | Crystals, isometric and quadratic. |
| Color, brilliant white. | |

**OCCURRENCE.**—Tin occurs chiefly as *tinstone, cassiterite,* or *native oxide,* $SnO_2$, which forms in very hard quadratic crystals, usually dissolved by the presence of ferric or manganic oxide. The pure ore is colorless and very scarce. Another native form known as "*wood tin*" occurs in roundish masses, with a fibrous, radiating fracture. The metal is rarely, if ever, found free. The ore is mined from veins or layers within the older crystalline rocks and slates, associated with copper ore, iron arsenide and other minerals, and as alluvial deposits, mixed with rounded pebbles, in the beds of streams. The former is called *mine-tin,* and the latter *stream-tin.* It is said that the Black Hills of Dakota contain 500 square miles of tin producing district, containing more tin than all the tin mines of the world.

**REDUCTION.**—The ore is first washed to separate it from earthy impurities, and then stamped, and again

washed to separate the lighter gangue. It is then roasted at a low heat to volatilize the arsenic and sulphur, without at the same time fusing the ore. The copper ore, *copper pyrites,* is, during this time, joined with subsequent exposure to air and moisture, changed to copper sulphate, and is then dissolved out by water, the copper afterwards being reduced by iron and thereby saved. The ore is finally washed to separate all lighter oxides, and is then ready for smelting. The purified ore, known as black "tin," is mixed with about 15 to 20 per cent of anthracite "smalls," the mixture moistened to prevent its being blown off by the draft, then fused in a reverberatory furnace for five or six hours, and, after thorough stirring, the metal is run off—

$$SnO_2 + 2C = Sn + 2CO.$$

The tin obtained from Malacca is almost chemically pure, while that from England almost invariably contains traces of arsenic and copper. Most of the tin consumed in this country is shipped from Singapore, having been mined in the Malacca regions. Two varieties of the commercial metal are known, called *grain* and *bar tin.* The first is the better; it is prepared from the stream ore.

**Pure Tin.**—Tin used in dental operations should be *chemically pure.* Much of that which we have just described is still greatly contaminated with arsenic, copper, iron, etc., and to obtain it pure a further refining process must be gone through with. For this purpose good commercial tin may be dissolved in hydrochloric acid. Hydrogen is evolved, and the metals are all converted into chlorides, with the exception of antimony

and arsenic. If either of these be present, it will combine with hydrogen, forming a gas and be evolved. The liquid is now evaporated to a small bulk, and to it is added nitric acid, which will convert the tin into the insoluble, white, crystalline, metastannic acid, $H_{10}Sn_5O_{15}$. The whole is now evaporated to dryness, washed with water acidulated with hydrochloric acid, filtered, rewashed, dried, and melted in a crucible with charcoal, when a button of pure tin will result.

**PROPERTIES.**—Pure tin is white (except for a slight tinge of blue); it exhibits considerable luster and is not subject to tarnishing on exposure to normal air. It is soft and exceedingly malleable; indeed, it is said it may be beaten into foil $\frac{1}{40}$ of a mm. in thickness; at 100° C. it may be drawn into wire, but it is almost devoid of tenacity. That it is elastic, within narrow limits, is proven by its clear ring when struck with a hard body under circumstances permitting free vibration. Though it is seemingly amorphous, it has a crystalline structure, hence the crackling noise known as the *"tin cry"* which a bar of tin emits on being bent. The crystalline structure must also account for the strange fact that an ingot, when exposed to the temperature of—39° C. for a sufficient length of time, becomes so brittle that it falls into powder under pestle or hammer. At some temperature near its fusing point it again becomes brittle. Tin fuses at 232° C. At a red heat it begins to volatilize slowly; at 1450° to 1600° C. it boils and may be distilled. The hot vapor produced combines with the oxygen of the air, forming the white oxide, $SnO_2$. The specific gravity is 7.29. Its specific heat is 0.0559.

**DENTAL APPLICATIONS.**—Tinfoil is very highly recommended as a filling material for carious teeth on account of the ease with which it may be inserted, its supposed therapeutic effect (which is doubtful), and because of its comparatively low conducting power of heat, tin as compared to silver, which is taken as the unit, being 15.2, while gold rises to 68, and absolutely pure gold much higher. In the conduction of electricity the comparison is still greater: tin 14.4 and gold 76.6. The combination of tin and gold foil is said to have a very low conducting power of heat. It is claimed that disintegration of the tooth structure by galvanic action at the margins of the cavity so filled is rendered impossible, from the fact that any such action is confined to the metals which form a closed circuit, tinfoil being more electropositive to gold than tooth structure. It is also claimed that consolidation of the two metals occurs subsequent to their insertion as a filling. Of this the late Dr. W. D. Miller says: "Without entering into a prolonged discussion of the causes of this consolidation, I will say that it is owing to electrochemical process, through which the tin is dissolved and redeposited upon the surface of the gold. By this means the material becomes rigid and all parts of the filling thoroughly bound together. * * * It has neither therapeutic nor antiseptic action."*

Casts of tin are used to vulcanize upon, and plaster casts are often covered with tin-foil to give a clear and finished appearance to the denture after the process of vulcanization.

**COMPOUNDS WITH OXYGEN.**—There are two oxides of tin:

*Cosmos, xxxii, p. 714.

**Tin Monoxide,** or *Stannous Oxide,* SnO, is a blackish-brown powder of feeble basic reaction prepared by heating stannous hydrate, Sn2HO, in an atmosphere of carbon dioxide. It is unstable, and burns when heated in the air, becoming stannic oxide.

**Tin Dioxide,** or *Stannic Oxide,* $SnO_2$, occurs native as tinstone, or cassiterite, the common ore of tin, and is easily formed by heating tin, stannous oxide, or stannous hydrate, in contact with air. According to the manner in which it may be prepared, it is either a white or yellowish-white amorphous *powder,* or it may be obtained *crystalline.* It is infusible and insoluble in the acids or alkalies, and is known as "polishing putty," being used for polishing glass, hard metals, granite, and similar substances. It forms two isomeric hydroxides (stannic and metastannic), which differ somewhat in their properties; both, however, are acids, and capable of exchanging their hydrogen for metal, thereby forming salts.

**Stannic Acid,** $H_2SnO_3$, is precipitated by an alkali from stannic chloride as a white powder, soluble in the stronger acids and alkalies, and is capable of exchanging the whole of its hydrogen for metal forming stannates, as: $Na_2SnO_3$. These salts are quite stable.

**Metastannic Acid,** $H_{10}Sn_5O_{15}$, may be written $H_2SnO_3$, is prepared as a white crystalline powder by the action of dilute nitric acid upon tin. It is insoluble in water and the acids, but dissolves slowly in the stronger alkalies, and has the property of exchanging only one-fifth of its hydrogen for metal-forming metastannates, very unstable, as $K_2H_8Sn_5O_{15}$.

**ACTION OF ACIDS ON TIN.**—The three mineral acids act upon tin.

**Sulphuric acid,** concentrated, acts rather energetically at first, but, owing to the stannic sulphate coating which is soon formed, its action is greatly hindered. The dilute form acts slowly, but converts the whole of the tin into stannic sulphate with a liberation of hydrogen.

$$Sn + H_2SO_4 = SnSO_4 + 2H.$$

**Nitric Acid.**—In its concentrated form this acid acts but feebly upon tin, and, if heated, produces the nitrate; but the dilute is energetic, and, instead of dissolving, *oxidizes* it into the crystalline powder, hydroxide, known as metastannic acid—$H_{10}Sn_5O_{15}$.

$$3Sn + 4HNO_3 = 3SnO_2 + 2H_2O + 4NO, \text{ and then}$$
$$5SnO_2 + 5H_2O = H_{10}Sn_5O_{15}.$$

**Hydrochloric Acid.**—Strong, warm hydrochloric acid acts energetically upon tin, the cold and dilute forms acting more slowly, but converting it into stannous chloride and liberating hydrogen.

$$Sn + 2HCl = SnCl_2 + 2H.$$

**Nitro-hydrochloric acid** dissolves tin very energetically, producing stannic chloride, $SnCl_4$.

$$Sn + 4Cl \text{ (nascent chlorine)} = SnCl_4.$$

**Caustic Alkalies.**—Boiling solutions of caustic soda or potassa act upon tin, producing stannates with an evolution of hydrogen.

$$Sn + 2KHO + H_2O = K_2SnO_3 + 4H.$$

**ALLOYS.—Mercury** and tin readily unite as an amalgam, under ordinary circumstances, and, it is said,

form a definite chemical compound having the formula, $Sn_2Hg$.

Tin is a very important component of dental-amalgam alloys.* Of it Dr. J. Foster Flagg says, in his work on *Plastics and Plastic Filling:* "All such alloys as I should favorably regard, have from 35 to 48 per cent of tin; it is found that by the addition of copper and gold, both antagonists of "shrinkage," the most deleterious of the effects of tin can be counterbalanced; that under this control sufficient silver can be used to obviate a detrimental loss of edge-strength; that the retardation of "setting" is prevented, and that the tin not only loses its power for harm, but becomes an ingredient of manifold utility; it greatly augments the facility of amalgamation; it aids in producing a good color and in preventing discoloration; and it diminishes conductivity."

The amalgam of tin is also largely used in the manufacture of mirrors.

**Gold** and tin form a malleable alloy, provided the tin be pure and does not exceed in quantity 10 per cent.

**Platinum** and tin in equal proportions form a hard, but brittle, alloy, fusing at a comparatively low temperature.

**Palladium,** says Mr. Makins, forms a very brittle alloy with tin.

In view of the fact that gold, platinum, and palladium so readily unite with tin to form alloys whose fusing points are so comparatively low, and in view of the behavior of tin with other metals, and of metals in general toward each other, there is little reason to

*See chapter on Amalgams.

doubt a chemical affinity of tin for these metals. The affinity of tin for gold in particular has been clearly demonstrated by Dr. Matthiessen. Into a crucible of molten tin a rod of gold and one of copper were dipped, the latter having been previously tinned to ensure perfect contact. The gold united readily and rapidly with the tin, while the copper rod remained unaffected. A gold wire which has been superficially tinned will melt like one of tin when held in the flame of a Bunsen burner. A wire of tinned copper exposed to the same heat, under like circumstances, remains unaffected, except that the tin is burned off. The affinity of tin for platinum is so great, states Clarke, that if tin and platinum foils be rolled together and heated before the blowpipe, combination takes place explosively. The affinity of tin for gold is unquestionably an interesting subject for the dentist, in view of the place these two metals occupy in operative dentistry.

**Silver** alloys with tin, and, in the proportion of 80 of the former to 20 of the latter, it is said produces a very tough alloy.

**Dr. G. F. Rees's alloy** for artificial dentures, constructed by the cheoplastic process, is composed of tin 20, gold 1, and silver 2 parts.* Other alloys much used in cheoplastic work are composed largely of tin.

**Bean's alloy,** intended for casting lower dentures, is composed of tin 95, and silver 5 parts.

**Antimony** 1 and tin 16 parts forms another alloy, which is intended for the same purpose, and was introduced by Dr. William B. Kingsbury.

*"Amalgams and Alloys Chemically Considered," by J. Morgan Howe, M.D., Transactions New York Odontological Society, 1880.

**Britannia metal** is made under a great variety of formulæ; one known as English is composed of antimony 7.8, tin 90.7, and copper 1.5. It sometimes contains lead or bismuth.

**Type metal,** generally speaking, consists of lead, antimony and tin—lead 55, antimony 30, and tin 15 parts.

**Dr. L. P. Haskell's Babbitt metal** for dies is composed of the following: "Copper 1 part, antimony 2 parts, tin 8 parts. These should be melted in the order named, as tin would oxidize badly before the first was melted, if all were placed in the crucible together. Melt, and turn off into ingots, and remelt. If it should not be found to run freely from the ladle, when making a die, add a small amount of tin, as it is presumable that some of that metal has oxidized."*

**Babbitt metal** is made under a great variety of formulæ; but one in the same proportions as the above (tin 12 parts, antimony 3 and copper 2 parts) is given by Dr. Essig, which, he states, is sometimes used in the dental laboratory for dies, and is thought by many to be superior to zinc for that purpose.†

**Copper** and tin form a large number of alloys of great importance.

**Bronze.**—Copper and tin unite in almost any proportion to form bronze.

| | Copper | Tin | Phosphorus | Zinc |
|---|---|---|---|---|
| U. S. Ordnance Bronze.. | 90. | 10. | ..... | ..... |
| Phosphor-Bronze ..... | 90.34 | 8.90 | 0.76 | ..... |
| Statuary Bronze ..... | 84.42 | 4.30 | ..... | 11.28 |

*Dr. L. P. Haskell.
†Dental Metallurgy.

**Actual speculum-metal** is supposed to have the formula, $Cu_4Sn$, and the centesimal composition of copper 66.6 parts and tin 33.4 parts.

**Bell metal** is copper 74 to 85 parts, and tin 26 to 15 parts.

**With iron,** in the process of tin-plate manufacture, tin is said to alloy.

**Lead** and tin alloy freely in all proportions, tin generally imparting greater resistance to the lead. The strongest alloy of lead and tin is Pb-1; Sn-3. Such alloys constitute certain forms of pewter, an important class called "soft solders," and counterdies.*

**TESTS FOR TIN IN SOLUTION.**—To the suspected solution add a few drops of **caustic potash** or **soda.** A white precipitate is thrown down, soluble in excess of the reagent.

**Ammonia** also gives a white precipitate *in*soluble in excess of the reagent.

**Ammonium** or **hydrogen-sulphide** throws down a brown, in the case of stannous, and yellowish-brown precipitate with stannic chloride, both of which are soluble in excess of the reagent.

**Gold trichloride** added to a dilute solution of the tin chlorides gives the characteristic purple precipitate, known as the purple of Cassius.†

**ELECTRODEPOSITION OF TIN.**—Tin is easily deposited upon small articles of brass or copper by simple immersion, as by the following experiment:

**EXPERIMENT No. 33.**—Place the articles in layers between sheets of tin foil in a saturated solution of potassium bitartrate

*See Lead Alloys.
†See chapter on Gold.

and boil. A little stannous chloride may also be added, if necessary.

The metal may be crystallized out of its solution and rendered pure by the following:

**EXPERIMENT No. 34.**—Immerse a bar of tin in a strong solution of stannous chloride and pour on carefully, so as not to disturb the tin solution, some distilled water. Pure tin will be deposited on the bar of tin at the point of junction of the water and tin solution.

# CHAPTER IX

## BISMUTH

| | |
|---|---|
| Bismuthum. | Symbol, Bi. |
| Valence, III, V. | Specific gravity, 9.7474. |
| Atomic weight, 208. | Malleability, brittle. |
| Melting point, 269. | Tenacity, brittle. |
| Ductility, brittle. | Chief ore, native metal. |
| Conductivity (heat), 1.77. | Conductivity (electricity), 1.4. |
| (Silver being 100.) | |
| Specific heat, 0.03013. | Crystals, rhombohedral. |
| Color, white with reddish tint. | |

**OCCURRENCE.**—Practically the only ore of this element is the *Native Metal* found disseminated in veins through slate rock associated with the ores of copper, iron, cobalt, nickel, silver, gold, and arsenic. It is a comparatively rare metal, inasmuch as the supply has not kept pace with the demand, and its commercial value has risen considerably. It is found chiefly in Saxony, Transylvania, United States, England, Peru, Norway and Sweden.

**REDUCTION.**—This is simple and may be accomplished by a process of sweating. The crushed ore is introduced into large iron tubular retorts, built in the furnace. These tubes are placed in an inclined position over a wood fire. At the upper end the ore is introduced, and as the metal is sweated out it accumulates at the lower end, where it is drawn off into iron vessels. The siliceous residue is then raked out of the tube at its upper end and the retort recharged.

Commercial bismuth frequently contains arsenic and iron, besides gold and silver, hence is not fit for dental usage until it is purified. When silver exists in bismuth in sufficient quantity to repay for extracting, it is cupellated just as lead is, while the bismuth is oxidized, leaving the silver as a molten button on the cupel. From the oxide the bismuth is afterwards recovered by strongly heating under powdered charcoal. At the same time the arsenic is got rid of, in that it volatilizes.

**PROPERTIES.**—Bismuth is a highly crystalline, hard, and very brittle metal, having a grayish-white color, with a decided reddish tint. Its specific gravity is 9.747 and fuses at 269° C. It expands about $\frac{1}{32}$ of its volume when solidification takes place and imparts this property to its alloys. It crystallizes in large, beautiful iridescent rhombohedra, which nearly approach a cube. These crystals may be obtained by melting a quantity of the metal and allowing the bulk to cool slowly, the surface being prevented from more rapid solidification by covering the pot with a sand bath filled with glowing coals. As soon as a crust has formed on the sides and top, it is pierced with a hot iron, and the still molten metal poured out. When quite cold the upper surface is sawed off, exposing the beautiful crystals in the interior. The metal volatilizes at a high temperature, and has a specific heat of 0.0301. It is the most diamagnetic of all substances. Exposed to the air at ordinary temperatures, it is unaffected, but when heated to a red heat it rapidly oxidizes, producing a beautiful play of colors.

**COMPOUNDS WITH OXYGEN.**—Bismuth combines with oxygen to form two stable oxides; $Bi_2O_3$ and

$Bi_2O_5$. The oxides $Bi_2O_2$ and $Bi_2O_4$ also may be formed.

**Bismuthous Oxide**, the *Trioxide*, $Bi_2O_3$ is found native as bismuth ochre, and may be prepared by roasting the metal in air or by gently igniting its nitrate. It is a straw-yellow powder, insoluble in water and fusible at a high temperature.

**Bismuthic Oxide**, the *Pentoxide*, $Bi_2O_5$, may be obtained by dissolving the trioxide in caustic potash and passing chlorine through the liquid; the water decomposes, forming hydrochloric acid, and the trioxide is converted into the pentoxide. It is then washed with dilute nitric acid to separate any remaining trioxide. The pentoxide is a reddish-brown powder, which is insoluble in water. The bismuthyl radical $-Bi=O$ acts like a monad, giving bismuthyl salts or the O may be replaced, giving normal salts.

**ACTION OF ACIDS ON BISMUTH.—Sulphuric acid** when cold has but slight action on bismuth, but dissolves it more readily when heated, forming the sulphate, and giving off sulphurous anhydride.

**Hydrochloric acid**, hot or cold, but feebly attacks bismuth.

**Nitric acid** dissolves bismuth very energetically, forming the nitrate or ternitrate, as it is generally termed, $Bi3NO_3$, which is a white crystalline, soluble mass.

If the ternitrate be added to a large quantity of water, a white precipitate is thrown down known as the subnitrate of bismuth, $BiONO_3$, which is much used in medicine and as pearl white or *blanc de fard* in cosmetics. It is a heavy white powder, insoluble in water or alcohol. It is darkened by sulphuretted hydrogen.

**ALLOYS.**—Bismuth unites readily with other metals, the alloys being remarkable for their ready fusibility,

and for their property of expanding on solidification. These two properties render it most valuable as an ingredient to alloys used for making casts or dies where it is essential to copy fine lines, and in alloys when a very low fusing point is desirable. A great many combinations of lead, tin, bismuth and cadmium produce alloys possessing the latter property, some fifty-eight* being known that fuse at or below 100° C., and an alloy of lead 25.00, tin 12.50, bismuth 50.00 and cadmium 12.50 will fuse at 55.5° C. Generally 50% of the low fusing alloy is bismuth. (See table p. 193.)

With **tin** bismuth alloys in any proportion. A very small quantity of the metal imparts to tin more hardness, sonorousness, luster, and a fusibility lower than either of the metals taken separately possesses. An alloy of equal parts of the two metals fuses at 212° C.

With **lead** bismuth alloys very easily, producing an alloy which is malleable if the proportion of bismuth does not exceed that of lead. The specific gravity is greater than the mean of the two taken separately. These alloys are white, lustrous, harder than lead, and more malleable† up to a certain proportion. Bismuth 1 and lead 2 gives a very ductile and malleable alloy fusing at 165.5° C. $3Pb + 2Bi$ forms an alloy having ten times the hardness and twenty times the tenacity of lead.

With **copper** it forms a pale-red, brittle alloy.

With **zinc** it easily unites; producing an alloy, sometimes employed in the dental laboratory for the formation of dies, such an alloy having a lower fusing point

†Jour. Soc. Chem. Ind., xxv, p. 1221.
*William T. Brannt.

than pure zinc, and being free from contraction on cooling.

| | Bi | Sb | Sn | Pb |
|---|---|---|---|---|
| Cliché-metal ..... | 9. | 10.5 | 48. | 32.5 |
| " Type-metal... | 8. | 1. | 4. | 5. |
| " " ... | 1. | 3. | ..... | 8. |

**Alloys of bismuth, tin, and lead** are known as the triple alloys, and are very numerous and useful.

**Newton's alloy,** improperly called "Melotte's Metal," consists of bismuth 8, lead 5, and tin 3 parts, and fuses at 94.4° C.

**Rose's fusible alloy** is composed of

| | I. | II. |
|---|---|---|
| Bismuth ..... | 2 | 8 parts |
| Tin ..... | 1 | 3 " |
| Lead ..... | 1 | 8 " |

The first fuses at 93° C. and the second at 94° C. They were used as safety-plates and inserted in the top of steam boilers, intended to prevent the explosion of boilers by allowing the steam to escape at a certain tension.

**Wood's metal** consists of lead 4, tin 2, bismuth 5 to 8, and cadmium 1 to 2, melts at 60° C. to 66.4° C., in color resembles platinum, and, is, to a certain extent, malleable.

**Onion's fusible alloy** contains lead 3, tin 2, and bismuth 5 parts, and melts at 91.6° C.

"La Nation" describes a fusible alloy, of which the following is the formula: Bismuth 48, cadmium 13,

lead 19, and tin 26. It melts at 70° C. and resists great pressure.

**Hodgen's fusible alloy,** for making dies and counterdies by the dipping process, is composed of the following: Bismuth 8, lead 5, tin 3, and antimony 2. It is a light, lustrous alloy, very hard, slightly malleable, expands slightly on cooling, copying the finest of lines, takes a high polish and resists great pressure, melting at 106.6° C.

**Dr. Mathews' Fusible Alloy.**—This alloy is composed of bismuth 48, cadmium 13, and tin 19 parts. It melts below the boiling point of water and may be packed with the fingers. It may be poured into plaster impressions immediately after they have been taken, producing sharp, bright, hard dies, with which shot may be used for the counterdie.

**Darcet's fusible alloys** are a series of proportions of bismuth, tin, and lead, and their melting point varies as per the following table:

| Parts | | | Melts |
|---|---|---|---|
| Bismuth | Tin | Lead | |
| 7 | 4 | 2 | 100° C. |
| 16 | 7 | 4 | 100° C. |
| 8 | 2 | 6 | 96° C. |

Most of these fusible alloys are of much value in the dental laboratory in the hands of a practical, resourceful man. The cleaner ones may, when lack of time will not permit of a more perfect repair, be used to mend a denture or replace a tooth or block of teeth on a vulcanite plate, and the more fusible ones may be used for the same purpose, even though the base be cel-

luloid. In replacing teeth undercuts may be made with a file, or preferably with a large bur in the engine, the tooth placed in position and the alloy packed in with warm instruments, smoothed and afterward polished. These alloys are also valuable baths for tempering steel instruments. They give a very exact temperature, which may be adjusted to the purpose intended. They are used, according to Thurston,* by placing the articles on the surface of the unmelted alloy and gradually heating until fusion occurs and they fall below the surface, at which moment their temperature is right; they are quickly removed and cooled in water.† "An alloy of 3 parts each bismuth, fine gold, and platinum with 15 of fine silver, and 10 of tin, is very similar to precipitated palladium, and has been used as a substitute for this costly metal. One curious point about this alloy is, asserts Mr. Fletcher, that if it contains the merest trace of palladium, it is almost worthless; and as ordinary fine silver is rarely, if ever, free from palladium, this alloy can only be made from silver reduced direct from the chloride."

In **amalgams.**—"The addition of bismuth to amalgams makes them excessively sticky and adhesive necessitating, at the same time, an increase in the proportion of mercury required."‡

The same author, continuing, says: "Amalgams containing a trace of bismuth will build and adhere to a flat dry surface, and may be used as a metallic cement for joints in apparatus which require to be perfectly air tight and to stand heavy pressures. A good alloy for this purpose is 1 bismuth, 15 tin, 15 silver, fused and filed up, and then mixed in the pro-

*Brasses, Bronzes, and other Alloys.
†Metallic Alloys, Brannt.
‡Dental Metallurgy, Thomas Fletcher, p. 65.

portion of 1 alloy to 4 of mercury. This alloy is so excessively sticky as to be useless for fillings."*

Commenting on the above, Dr. Kirk says:† "The effect of bismuth in dental-amalgam alloys does not seem to have been fully studied." And, further, "it would seem that the power of bismuth to overcome the contraction of alloys in solidifying would render it valuable as an ingredient in certain dental-amalgam alloys if it conferred no objectionable qualities other than adhesiveness upon them."

**TESTS FOR BISMUTH IN SOLUTION.**—Makins states: "The salts of this metal are for the most part devoid of color; some are soluble, others insoluble, the soluble salts redden litmus paper."

**Sulphuretted hydrogen** or **ammonium sulphide** when added to a solution produces a black precipitate—sulphide of bismuth—insoluble in dilute acids or alkalies, but dissolves in strong hot nitric acid.

The alkalies *precipitate* from bismuth solutions—in the absence of certain organic substances—the white bismuth hydrate, Bi3HO, insoluble in excess of the reagents, converted by boiling to the yellowish-white oxide, $Bi_2O_3$.

**The carbonates**—as $K_2CO_3$—precipitate the white basic bismuth carbonate, $Bi_2O_2CO_3$, insoluble in excess of the reagents.

**Water** precipitates from acidulated bismuth solutions white basic salts, which contain less of their acid radicals in proportion as greater quantities of water are added, as—

1. $Bi3No_3 + 2H_2O = BiONO_3. + H_2O + 2HNO_3.$
2. $4Bi3NO_3 + 6H_2O = Bi_4O_52NO_3. + H_2O + 10HNO_3.$

*Dental Metallurgy, Thomas Fletcher, p. 65.
†American System of Dentistry, iii, p. 931.

# CHAPTER X

## ZINC

| | |
|---|---|
| Zincum. | Symbol, Zn. |
| Valence, II. | Specific gravity, 7.142 at 16°. |
| Atomic weight, 65.37. | Malleability, 8th rank. |
| Melting point, 419° C. | Tenacity, 6th rank. |
| Ductility, 8th rank. | Chief ore, calamine. |
| Specific heat, 0.09356. | Crystals, rhombohedral. |
| Conductivity (heat), 26.53. | Conductivity (electricity), 29.6. |
| Color, bluish-white. | |

(Silver being 100.)

**OCCURRENCE.**—Zinc is a somewhat abundant metal, but never occurs in the native state. It is found as a carbonate, sulphide, silicate, etc., associated with lead ores in many districts; large supplies are obtained from Silesia and from the neighborhood of Aachen.

(1) The native carbonate, *Calamine,* Smithsonite, $ZnCO_3$, is the most important of its ores. As a rule this ore is a light-gray, yellow, or buff in color. (2) *Zinc blende,* the sulphide, ZnS, is second in importance only to the carbonate; it is extensively mined and much of the zinc of commerce is procured from this ore. Its color is green, yellow or red but mostly brown. There is also a (3) *Red Zinc Ore,* an impure oxide, ZnO; an (4) *Electric Calamine,* one of the silicates, $ZnO.SiO_2 + H_2O$ and (5) Willemite, an anhydrous silicate, $ZnO.SiO_2$.

**REDUCTION.**—Calamine, $ZnCO_3$, is generally reduced by first roasting, to expel the water and carbon

dioxide. This leaves the oxide, ZnO, which is then mixed with fragments of coke or charcoal, and distilled at a full red heat in a large earthen retort. The carbon unites with the oxygen to form carbon monoxide and escapes, while the reduced metal volatilizes and is condensed by suitable means, generally contaminated with minute quantities of arsenic. Metals having a lower boiling point such as cadmium, arsenic, lead and antimony, come over first and with some zinc form what is known as zinc dust largely used in paints. Zinc blende is roasted to drive off the sulphur, but

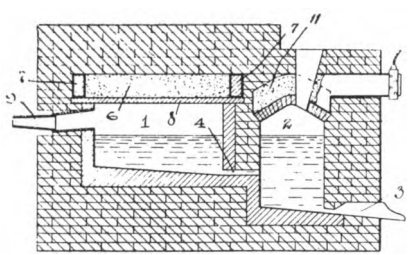


Fig. 39.—A furnace for purifying zinc. Patented by Richard Ziesing. Consists of two chambers *1* and *2*. It may be heated in any manner though this type is heated by resistance elements at *6* and *11* in the diagram. Zinc contaminated with impurities having a heavier sp. gr. is charged into chamber *2* through the hopper, and heated until the molten metal nearly reaches the level of the outlet to the condensing chambers at *9*. During this time the heavier metals sink to the bottom and are drawn off at *3*. When the furnace is fully charged, the temperature is increased and the metal is distilled over at *9* and condensed in metallic form.

when it contains any foreign sulphide, as of lead, it is more difficult and requires several hours roasting.

Old zinc may be refined or cleansed for use again in the laboratory by heating with pulverized charcoal or some hydrocarbon, as wax, etc.

**PROPERTIES.**—Zinc is a bluish-white metal, which but slowly tarnishes in moist air, usually forming a superficial carbonate which prevents further disinte-

gration; it has a lamellar, crystalline structure, a specific gravity of 7.142, and is, under ordinary circumstances, quite brittle, but when heated to 100° or 150° C. it may be rolled by passing through heated rolls or hammered into thin sheets, or drawn into wire; and, what is very remarkable after such treatment, it retains its malleability when cold; the sheet zinc of commerce is thus made. The addition of any of the following metals is harmful to sheet zinc during manufacture: Cd. 0.25%; As, 0.02—0.03% impossible to work; Sb 0.07%; Sn 0.01%; Cu 0.08—0.19% unworkable; Fe, 0.12%; Pb, 1.00—1.25% does not interfere, but does not alloy, leaving patches. If the temperature be carried to 205° C. it again becomes so brittle that it may be easily powdered in a mortar. Care should be exercised in handling hot zinc dies, for if by accident one be dropped upon a hard surface it is likely to be ruined. The metal melts at 419° C. It boils at 918° C. and, if air be admitted, burns with a splendid greenish incandescence, forming the oxide. In boiling water zinc is said to be attacked appreciably, but no more, forming the hydroxide, Zn2HO, with evolution of hydrogen. Zinc is electro-positive to all ordinary metals except aluminum and therefore will precipitate most of these metals out of their salt solutions. Possessing distinct galvanic properties, it is extensively used in both wet and dry batteries and its use in the mouth in any form influences galvanic action.

Zinc is ionized in simple and complex form, the former being $Zn^{++}$ while the latter we have the zincate ion $ZnO^{--}$ and zinc ammonia ions. $Zn(NH_3)_n^{++}$. The hydroxyl ion in combination with a zinc salt in solution, precipitates white $Zn\ O_2H_2$ which exhibits both acidic

and basic properties, for it may dissociate into $Zn^{++}$ and $(OH)_2^{--}$ ions, in which case the Zn ions act as metallic ions or it may dissociate into $H_2^{++}$ ions and $ZnO_2^{--}$ ions in which case zinc acts as an acid forming element.

$$\overset{++}{Zn}\,\overset{--}{O_2}H_2 + 2\overset{+}{H} - \overset{-}{Cl} = \overset{++}{Zn}\,\overset{--}{Cl_2} + \overset{++}{H_2}(\overset{--}{OH})_2 \text{ or } 2H_2O$$

$$\overset{++}{Zn}\,\overset{--}{O_2}H_2 + 2\overset{+}{Na}\overset{--}{OH} = \begin{matrix}\overset{+}{Na}-\overset{--}{O}\\ \overset{+}{Na}-\overset{--}{O}\end{matrix}\!\!>Zn + \overset{++}{H_2}(\overset{--}{OH})_2 \text{ or } 2H_2O$$

The phosphate ion $(\overset{---}{PO_4})$ precipitates white $Zn_3(PO_4)_2$ which is quite soluble in acids even in acetic acid. The chloride ion Cl – produces no precipitate. $ZnCl_2$ is so extremely soluble that it melts in its own water of crystallization or being hygroscopic quickly absorbs moisture from the air and on going into solution tends to become cloudy, due to hydrolysis forming the basic salt $Zn\begin{matrix}OH\\Cl\end{matrix}$.

$$Zn\begin{matrix}Cl\\Cl\end{matrix} + HHO = Zn\begin{matrix}OH\\Cl\end{matrix} + HCl$$

a basic chloride.

$$Zn\begin{matrix}OH\\Cl\end{matrix} + HHO = Zn\begin{matrix}OH\\OH\end{matrix} + HCl : Zn\begin{matrix}OH\\OH\end{matrix} + \text{heat} = ZnO + H_2O.$$

**IN THE ARTS.**—Zinc meets with extensive application. It is much used for the positive element in galvanic batteries, and in the form of sheet zinc it is greatly employed in manufacturing industries.

**DENTAL APPLICATIONS.**—Zinc has long been very extensively used in the dental laboratory for making dies. Its comparatively low fusibility, hardness, and other properties eminently fit it for this purpose.

**DIES.**—"In passing from a low to a higher temperature zinc increases in volume in a greater ratio than any of the metals in common use. The coefficient of its cubical expansion between zero and 100° C., which represents the rate of increase of its unit volume between these temperatures, has been found to be 0.000088251, or nearly three times that of cast iron. The rate of expansion of liquids being greater than that of solids, and as this rate is not constant, but increases with the temperature, the rate of increase in volume which zinc undergoes in passing from the solid to the fluid condition would be represented by a figure somewhat higher than that given above. From the fact that metal plates for entire dentures which have been swaged upon dies made of zinc generally fail to fit the plaster model accurately, it is held by some practitioners that the high rate of expansibility of zinc is an undesirable feature; but as the absolute contraction in the size of a zinc die is but slight, and as the difference in the size of a plate made upon it and that of the mouth for which it is intended is to a certain extent reduced or counteracted by the expansion which the plaster model undergoes in setting, it is questionable whether the contraction which takes place in zinc on passing from the fluid to the solid condition is of any detriment. It is held by many, and for potent reasons, that in most cases the contraction which occurs in a zinc die is of positive benefit. A plate swaged upon a zinc die is, by reason of the contraction which

the metal undergoes in passing from the fluid to the solid state, slightly smaller than the mouth it is intended to fit, thus bringing the greatest pressure to bear upon the alveolar ridge. Should the plate be made to fit upon the plaster cast, it would be a trifle larger than the mouth, as plaster expands in setting, and two expansions have taken place in taking the impression and making the cast. The pressure exerted by such a plate would be expended upon the bony arch of the hard palate. Usually the tissues covering the alveolar ridge are thicker, and therefore more yielding, than those covering the hard palate, and a plate swaged upon a zinc die would be of positive advantage, as the slight absorption of the tissues covering the alveolar ridge which result from the increased pressure, would soon bring about a perfectly uniform bearing over the entire area covered by the plate. But one class of cases arises, and their occurrence is infrequent, where the quality of expansibility of zinc is detrimental to the fit of a plate when swaged upon it—namely, where the tissues covering the bony arch of the hard palate are thick and spongy, while the alveolar ridge is hard and covered by a thin unyielding membrane. When this set of conditions presents, it is usually in combination with a high V-shaped arch. In such cases a die of Babbitt metal gives better results, though even with a zinc die the difficulty can be readily overcome and a proper adaptation secured by properly manipulating the plaster cast or impression, i. e., by scraping those portions of the cast which represent the soft, yielding portions, or by treating the impression in like manner at those

positions which represent the hard or unyielding parts of the ridge."*

**Counterdies.**—Zinc is frequently used for making the counterdie as well; being hard and unyielding, copying the finest lines, it secures a perfect and ready adaptation of the metal to the die. In working platinum-gold or iridio-platinum the lead die is entirely inadequate to perfectly swage the metal to the die, especially where the palatine arch is very high or the rugæ prominent, and it is then that a zinc counterdie is especially serviceable. It is also of great assistance in conforming plates to dies for partial dentures, as it more perfectly forces the metal snugly about the necks of the teeth than lead can be made to do.

The zinc counter is formed similarly to the manner of making a lead counter, except that the die should be quite cool†—not cold—and thinly coated with a solution of whiting, which is allowed to dry, or with a deposit of carbon, obtained by smoking the die over a candle flame. In experienced hands the coating may be dispensed with and zinc heated *just to complete fusion, and quickly poured in an uninterrupted stream* upon the cool die.

Dr. Essig‡ recommends, where swaging is likely to be attended with difficulty, "at least three sets of dies and counterdies." With the less perfect of the dies he pours a lead counterdie and uses it for the preliminary swaging of the metal to the die. A partial lead counter is also exceedingly serviceable in the preliminary con-

*Dr. E. C. Kirk, Am. System of Dentistry, iii, p. 922.

†If melted zinc is poured at 427° C. upon a zinc die at 21° C., the fused zinc by contact with the iron ring and by radiation will lose heat enough to cause its temperature to fall far below the fusing-point, and it will probably not impart to the die more than 204° C.—Essig.

‡Dental Metallurgy, p. 232.

formation of the plate to the buccal and labial portions of the process. Such a counter is held in position by various means, the most practical of which, that has come to the writer's notice, is one used by Dr. Thomas N. Iglehart, consisting of a large steel screw-clamp, the bow of which may be represented by the letter U laid on one side, thus ⊂. The end of the lower side terminates in a large circular section of iron, provided with a flat base, perforated for screwing into the bench. The upper arm carries a screw, similar to those used in letter presses, and when the die is placed on the heavy iron below, the screw centers the partial counter from above, thus holding the two in a perfect grip, permitting swaging with the hammer or tracer all around. Such a device is especially serviceable in turning the rim. A second die is furnished with a zinc counter, and when the plate is so far conformed to the shape of the die as to preclude all probable wrinkling or folding, this counter is adjusted and the plate more perfectly driven to the die and the finer lines accurately copied. As the die is necessarily much marred by the unyielding quality of the counter, a third and very perfect die provided with a lead counter should be used to complete the swaging. The writer prefers to put the counterdie down finally under a steady pressure of from 1000 to 5000 pounds by means of a screw press.

**ZINC OXIDE.**—ZnO is the only known compound of this metal and oxygen. It is a strong base, forming salts isomorphous with those of magnesium. It may be prepared by heating the metal to 918° C., exposed to the action of the atmospheric oxygen. Soon after melting it begins to be covered with a film of gray

oxide. Just before the temperature reaches redness it takes fire and burns with an intense greenish-white light, forming a very light, white, flocculent oxide resembling carded wool, which quickly fills the crucible, and is in part driven into the atmosphere by the current of air. It may also be prepared by heating the carbonate, $ZnCO_3$, to redness, driving off the water and carbon dioxide, $CO_2$. Too high a temperature will

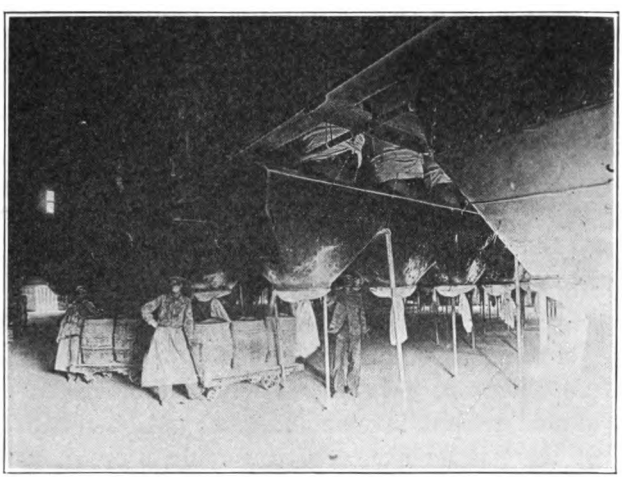


Fig. 40.—The interior of a bag house where the oxides of metals, particularly of zinc, are collected for commercial use. The metals are oxidized in a roasting or reverberatory furnace. Passing through long horizontal stacks to be cooled, finally reaching the bag house where the oxides are collected in bags from 25 to 50 feet long and 2 feet in diameter, the bases being attached to metal bins. Most of the zinc oxide of commerce is obtained in this manner.

discolor the oxide a light yellow, and, partially vitrifying it, will give to it a harsh, gritty feel. A good quality should present a soft, white, flaky, impalpable, amorphous powder, permanent in air, odorless and tasteless, insoluble in water or alcohol, but soluble in

acids without effervescence; also soluble in ammonia-water and ammonium carbonate solutions. When strongly heated (calcined), the oxide assumes a deep lemon color, but turns nearly white again on cooling. At a low white heat it fuses, and at a full whiteness sublimes. If it be contaminated with white lead or chalk, it will not be entirely soluble in dilute sulphuric acid, but an insoluble sulphate of lead or of lime will remain. If zinc oxide exhibits any effervescence on the addition of hydrochloric acid, a content of zinc carbonate is suspected and its presence is probably due to improper calcining.

**ZINC CEMENTS.**—No material is more generally used in dentistry than dental cements, and of all classes the zinc phosphates are the most common. They are most frequently spoken of as zinc oxyphosphates which is a misnomer, for there is no salt of zinc exhibiting a formula which would comprehend such terminology. From all chemical evidence obtainable we have, in mixing zinc oxide and phosphoric acid, a salt, viz., zinc phosphate or phosphite. If there is an excess of acid present, it remains as such until neutralized, and if there is an excess of the oxide present, it remains as such, probably accounting for the above term, oxyphosphates.

Since this material is of such importance, it is well to bear in mind the physical and chemical properties of the elements which go to make up dental cements.* The oxide of zinc is found in nature at Franklin Furnace, N. J., where it is extensively mined. It is prepared commercially by heating the hydroxide, carbonate, nitrate, sulphide, or acetate, or by heating the

*See properties of zinc and copper.

metal to 918° C. in the presence of air. For commercial purposes the latter is the customary method of preparation, for medicinal purposes it is prepared by heating the carbonate, and for dental purposes it is prepared, according to some authorities, by heating the nitrate, it being stated that an oxide of heavier specific gravity is thus obtained.

Zinc oxide is an amorphous, white, tasteless powder, insoluble in water, and when in a pure dry state is absolutely neutral in reaction. It is soluble in all the solvents of the pure metal, thus differing from the oxides of the other common metals. For dental cements, zinc oxide is calcined at a temperature of about 1400° C. for several hours. Usually an electric furnace of the muffle type, specially designed for this purpose, is used since it protects the oxide from possible contamination with the products of combustion.* Dr. Marcus L. Ward conducted a series of interesting experiments on cements in 1914-15, which have cleared up our hazy knowledge of the subject. He found by analysis and synthesis that the powder of the principally used cements, (Ames, Justi's, Fellowship, and Caulk's) consisted of zinc oxide with traces of silicon oxide and magnesium oxide, except that Caulk's Petroid was modified by the addition of magnesium oxide and bismuth oxide, (ZnO, 84., MgO, 10., $BiO_3$, 6.) and a trace of ferric oxide.

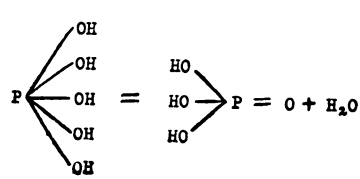
After calcination the oxide is found to be greatly contracted in mass, semivitreous, and the color has changed to a light yellow, which is probably due to a partial fusion. Ward states that calcining from eight to fourteen hours is the period of time best suited to

*Jour. N. D. A., ii, pp. 354-370.

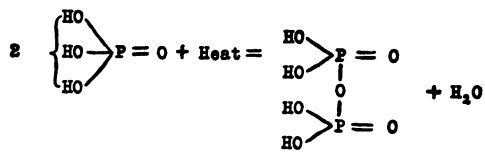
duplicate the manufactured products, the temperature approximating 1400° C. Also, that the longer the zinc oxide was fired, the slower it reacted with the cement liquids. The calcined mass is then reduced to a powder in a ball-mill, and bolted through bolting cloth, depending upon the service for which the cement is to be used, the coarser grades being used for filling purposes, and the finer grades being used for setting inlays.

Color modifications are produced by adding various oxides, as ferric oxide, cobalt oxide, copper oxide, which in themselves possess certain cement making properties. It is quite generally understood that the permanent yellow tints in zinc cement powders are not obtained wholly by calcination.

**ORTHOPHOSPHORIC ACID** is the acid used chiefly in zinc cements. Phosphorous in combination with oxygen forms $P_2O_3$ and $P_2O_5$ besides the lesser important oxides $P_4O$ and $P_2O_4$. $P_2O_3$ is an acid anhydride and with water readily forms metaphosphoric acid, $HPO_3$. It also combines with two more atoms of oxygen to form the pentoxide $P_2O_5$ which has such a strong affinity for water that it is the best dehydrating agent known to science. When the pentoxide and water stand for a long time a pentahydroxide $[P(OH)_5]_2$ is formed which forms orthophosphoric acid quite readily when attempts to isolate it are made.



If this compound be gently heated to about 255° C., it loses water and forms pyrophosphoric acid.



Heating pyrophosphoric acid gives two molecules of metaphosphoric acid and water.

Orthophosphoric acid, the most common type, is made by adding nitric acid to phosphorus and heating, gradually adding more acid until all the phosphorus has been oxidized.

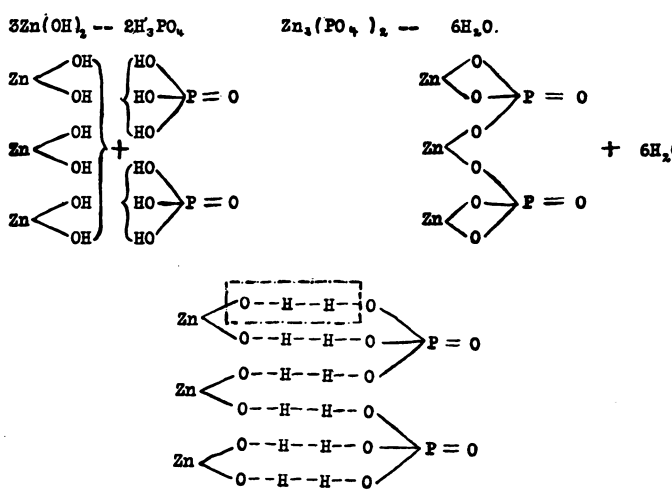
$$5HNO_3 + 3P + 2H_2O = 3H_3PO_4 + 5NO.$$

Glacial phosphoric acid, formerly used for the manufacture of cement liquids, is made by volatilizing metaphosphoric acid and condensing the vapors. The commercial product is made by adding sodium metaphosphate, in some instances nearly sixty per cent, to metaphosphoric acid, to give hardness and transparency. Orthophosphoric acid may be obtained from this by adding distilled water and boiling down, when the meta compound takes up water to form the ortho compound, with sodium metaphosphate still present.

Dr. Ward found that the liquids of the most commonly used cements consist of orthophosphoric acid, modified by the addition of hydrated aluminum oxide and water in varying proportions, depending on the rapidity or slowness of setting desired. Poetschke states that occasionally salts of nickel and iron, and oxides of bismuth and magnesium are added as modifiers.

Since zinc produces only one series of compounds, it is logical to suppose that no matter which phosphoric acid is used, the ultimate phosphate formed will be $Zn_3 (PO_4)_2$ if the reaction runs to completion. It has been stated that a basic salt is formed. A basic salt is one that partakes more of basic properties than acid or neutral. How can we form a basic salt from a bivalent compound and a trivalent acid? There are three replaceable hydrogen atoms in orthophosphoric acid. Since zinc in an aqueous solution tends to decompose the water and form $Zn\ O_2H_2$, and since we use an aqueous or diluted solution of orthophosphoric acid, the following reactions may express graphically the several changes which take place in the production of a normal phosphate of zinc by the addition of small quantities of zinc oxide to orthophosphoric acid.

The basic salt therefore must be an excess of zinc oxide in combination with the normal phosphate.



Thus in the elimination of six molecules of water, by gradually incorporating the powder into the liquid, as shown above, we may produce five different salts of zinc before the normal phosphate is formed. Dr. Ames states that different grades of basic phosphate require different amounts of water of crystallization, and that in proportion to the normal phosphate formed during the mix, will the setting be retarded or modified. Segerblom gives us five phosphatic compounds of zinc:

1. $Zn(H_2PO_4)_2$, $2H_2O$., acid zinc phosphate.
2. $Zn(PO_3)_2$, $4H_2O$., zinc metaphosphate.
3. $Zn_2P_2O_7$, zinc pyrophosphate.
4. X, ZnO, Y, $P_2O_5$, Z, $H_2O$, basic zinc phosphate.
5. $2ZnHPO_3$, $5H_2O$., zinc phosphite.

The last one only is readily soluble in water.

**MIXING CEMENTS.**—The technic of mixing cements is very easily acquired. It does not require precision or strength or delicate manipulative skill, but it does require attention to detail and careful handling of the materials in hand. We are dealing with a chemical problem in a physical way. The end products would be just about the same if we poured a bottle of cement powder into a bottle of cement liquid, but the material could not be used for the purposes for which it was intended. It requires manipulation in order to render the mass plastic and thereby adapted to our needs.

Definite orders of procedure should be established. First, use a clean polished plate glass slab, free from scratches and ground surfaces and heavy enough to permit of mixing a creamy mix without holding it if

the occasion demands it. Any accumulation of cement crystals from a previous mix, that may remain on the surface or in the scratches, materially hastens the setting of a new mix. Second: use a broad stiff spatula, preferably of one of the nickel, copper, zinc alloys, variously known as German Silver, Nickel Silver, or Platinoid, or a bone or agate spatula, the latter being especially indicated for the siliceous cements. Steel spatulas are so readily oxidized by the cement liquids that they modify the color of the cement to a considerable degree, and may bring about a failure in setting porcelain inlays.

Third: the liquid, which should be kept in a special bottle with a telescoping ground glass stopper, is placed on the slab, by means of a glass stirring rod which can be washed after each operation. The accumulation of crystals around a common cork or in a pipette are unsightly and tend to modify the setting qualities of the liquid. Fourth: the powder should be kept in a well corked bottle at all times, for zinc oxide, as do all oxides, absorbs carbon dioxide from the air, and we are then dealing with a carbonate instead of the oxide, with unsatisfactory results. Place the powder on the clean slab and divide it into four or five portions. Then incorporate one portion at a time, thoroughly spatulating the mass until it is homogeneous before adding a second portion. Continue in this way until the desired consistency is obtained. The rationale of this process is to produce as large a quantity of normal zinc phosphate as is possible, to retard the setting and give time for manipulation. If we add a large amount of powder to the liquid with very little spatulation, we produce a large amount of

basic zinc phosphate which hastens setting and gives a flaky or clotty mix. If under such conditions we resort to excessive spatulation we may produce an excess of normal phosphate and retard the setting disastrously. It is better to discard the mix.

If, on the other hand, we do not add enough powder to thoroughly neutralize the liquid, we will have an acid phosphate, with the possibility of some free acid remaining which is very likely to attack the tooth structure as well as lessening the cementing qualities of the mix. In the end we have a mixture consisting of zinc and other oxides held by an agglomerating medium, normal zinc phosphate, provided the liquid is fully saturated by the powder.

Other classes of cements include chiefly copper cements and siliceous cements. The former are either the black oxide of copper (cupric) or the red oxide (cuprous) or a combination of either of these with zinc oxide, or zinc oxide modified by the addition of cuprous iodide ($Cu_2I_2$), cupric phosphate ($CuHPO_4$), or cupric silicate, ($CuSiO_3$). They are primarily intended for use in the deciduous teeth, for which they are particularly suited, and while much is claimed for their germicidal value, they should not be relied upon as germicides, *per se*. The siliceous cements are compounds of calcium and aluminum silicates, with in one instance a silicate of a rare element. The liquids are similar to the liquids used for the zinc cements, the chief difference being in the modifying agents. Little experimental work has yet been done by the profession on this problem. Properly manipulated, these compounds are more durable than the other classes of cements and they harmonize with the tooth structure

and color better. They are unaffected by the acids or alkalies, except sulphuric acid, and the various kinds of powders and liquids are interchangeable. This may be determined by simple experimental mixes.

**ACTION OF ACIDS ON ZINC.**—Pure zinc dissolves very slowly in acids or alkalies, unless in contact with copper, platinum, or some less positive metal. Any metallic impurity in zinc renders it quite soluble in the acids or alkalies. It is rapidly oxidized in water containing air, when in contact with iron, but the water does not dissolve it, unless aided by certain salts. All agents which dissolve the metal, also dissolve its oxide and hydroxide.

**In Sulphuric acid** dilute, it dissolves slowly, forming zinc sulphate, and evolving hydrogen.

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

In strong sulphuric a coating of zinc sulphate is quickly formed over the metal, retarding, if not altogether preventing further action.

**In Hydrochloric acid** it is also slowly dissolved when pure, more rapidly when contaminated, forming the chloride of zinc and evolving hydrogen—

$$Zn + 2HCl = ZnCl_2 + H_2.$$

**The Chloride** is a nearly white, translucent, fusible substance, very soluble in water and alcohol, and very deliquescent. It is used in dentistry when melted, or melted and diluted as liquid for oxychloride cement; as an obtundent to sensitive dentine, an antiseptic, disinfectant, etc.

**In Acetic acid** zinc slowly dissolves, forming the acetate, and evolving hydrogen—

$$Zn + 2HC_2H_3O_2 = Zn(C_2H_3O_2)_2 + H_2.$$

**In Nitric Acid.**—In very dilute nitric acid it dissolves without evolution of gas—

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + H_4NNO_3 + 3H_2O,$$

forming the nitrates of ammonium and zinc.

In moderately dilute cold nitric acid, it dissolves with evolution of nitrous oxide—

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + N_2O + 5H_2O.$$

In a less dilution it dissolves with evolution of nitric oxide—

$$3Zn + 8HNO_3 = 3Zn(NO_3)_2 + 2NO + 4H_2O.$$

In concentrated nitric acid zinc is but slightly soluble.

**IN ALKALIES.—In Potassium Hydrate,** and in all the caustic alkalies, zinc slowly dissolves, evolving hydrogen—

$$Zn + 2KHO = K_2OZnO + H_2.$$

**ALLOYS.—Mercury** and zinc amalgamate quite readily to form a definite compound, having the formula $Zn_2Hg$.*

**With Gold,** zinc readily unites. The malleability, brilliancy, and color of gold is impaired by a content of zinc.

**Platinum.**—Small pieces of platinum may be dissolved in molten zinc, and the union is attended with

*See chapter on Amalgams.

considerable energy, owing to the formation of a definite chemical compound. The alloy is hard and brittle. An alloy may be prepared of platinum, 16; copper, 7; and zinc, 1; which very much resembles gold in color, specific gravity and ductility.

**Silver** and zinc have a great affinity for each other. This fact, with the knowledge that zinc and lead are so comparatively incompatible, led to the process of desilvering lead by the assistance of zinc. The alloy of silver and zinc is best obtained by throwing the required quantity of zinc wrapped in paper into molten silver, stirring thoroughly with an iron rod, and pouring the fused mass at once. The alloy of two parts zinc and one part silver is flexible, ductile, and has nearly the color of pure silver. Larger proportions of zinc produce brittle alloys.

**Copper and Zinc Alloys.**—(See chapter on Copper.)

**Iron** and zinc unite to form a very interesting as well as somewhat useful and brittle alloy. Iron plate and ware when perfectly cleaned may be immersed in molten zinc and the surface alloyed slightly, forming what is known as "galvanized iron."* Zinc *alloys with* the iron melting pots of the laboratory; the admixture rendering the zinc less fluid when molten and more difficult to fuse. This contamination may be prevented by coating the pot with whiting.

**With Lead** zinc does not alloy, except to a very slight degree. "Matthiessen found† that on melting equal parts of zinc and lead, and, after well mixing, allowing the alloy to cool slowly, they separate, but the heavier

*See chapter on Iron.
†Makins' Metallurgy, p. 62.

lead on subsiding retains 1.6 per cent of the zinc alloyed with it; while, on the other hand, the upper layer of zinc thrown out retains 1.2 per cent of lead."

It often occurs that lead and zinc will become mixed in the laboratory, and is seldom discovered until the molten mixture is poured. Then the lead, owing to its greater specific gravity, falls to the bottom of the mold, forming the alveolar ridge of the die, rendering it worthless. Many times the counterdie is poured before the mistake is noticed, resulting in a union of the die and counterdie.

**Tin** and zinc alloy in almost any proportion. Mr. Fletcher recommends an alloy of zinc 2 parts and tin 1 part for making dies for swaging, claiming the impression from the sand is much finer, and the shrinkage on cooling is greatly reduced. It melts much lower than zinc alone, hence some care must be exercised in pouring the counterdie. The die should be perfectly cold and the lead should be just hot enough to pour, but not sufficiently heated to char a slip of paper.

**Bismuth and zinc** are almost immiscible in either a solid or liquid state except in alloys having less than three per cent of zinc by weight. Other alloys will not mix under 800° C.

**Cadmium and zinc** are miscible in all proportions in a liquid state, and they unite to form a definite chemical compound. An eutectic of Zn, 82.4; Cd, 17.6, melts at 260° C.

**TEST FOR ZINC IN SOLUTION.—The Caustic Alkalies** all precipitate the white hydroxide of zinc, Zn2HO, soluble in excess of either precipitant with the formation of sodium zinc oxide, etc.

$$ZnCl_2 + 2NaHO = Zn2HO + 2NaCl.$$
$$Zn2HO + 2NaHO = Na_2OZnO + 2H_2O.$$

**Ammonium sulphide** completely precipitates zinc as a sulphide.

**Alkaline carbonates** precipitate it as basic carbonate soluble in ammonia.

# CHAPTER XI

## CADMIUM

| Cadmium. | Symbol, Cd. |
|---|---|
| Valence, II. | Specific gravity, 8.642 at 17°. |
| Atomic weight, 112.40. | Malleability, 10th rank. |
| Melting point, 321.7° C. | Ductility, 11th rank. |
| Tenacity, 9th rank. | Chief ore, greenockite. |
| Specific heat, 0.0548. | Crystals, octahedral. |
| Conductivity (heat), 22.13. | Conductivity (electricity), 24.4. |
| Color, tin-white. | |

(Silver being 100.)

**OCCURRENCE.**—This metal does not occur native. There is but one mineral known which could be called an ore of cadmium, and which contains it in any quantity; namely, the sulphide, CdS, *greenockite,* which is found near Bishopstown, Renfrewshire. This ore is crystalline, belonging to the hexagonal system, and is of an orange-yellow color. Cadmium is, however, often associated with the zinc blende, ZnS, and Calamine $ZnCO_3$, and from these two ores it is principally obtained, varying in amount from 1 to 5 per cent. Practically the entire output in the United States comes from the zinc ores found in the Joplin district in Missouri, which contain about 0.3 per cent of cadmium. The metal very much resembles zinc, especially in its chemical properties.

**REDUCTION.**—A humid method (Stromeyer's) is to dissolve the zinc ore containing cadmium in dilute sulphuric acid and precipitate the metal as the orange-yellow sulphide by means of sulphuretted hydrogen.

The sulphide is then dissolved in hydrochloric acid, the excess of the solvent evaporated, and the cadmium thrown down as the carbonate by adding ammonium carbonate. By heating this to redness the carbon dioxide is driven off, leaving the oxide, which is mixed with carbon and distilled from an earthen retort. Most of the cadmium on the market, however, is obtained by roasting the zinc ores below the volatilizing point of zinc, usually during the first hour and a half. The retorting is frequently repeated to obtain the cadmium.

**PROPERTIES.**—Cadmium is a tin-white lustrous metal, tough, very volatile (next to mercury), and somewhat harder than tin, which it very much resembles physically. It fuses at 321.7° C. and boils at 778° C., giving off a yellowish-brown colored vapor. Its specific heat is 0.0548, electric conductivity somewhat lower than that of zinc, and its specific gravity 8.642 at 17°. It is malleable, ductile, and somewhat tenacious, breaking under an increasing strain, with fibrous scaly fracture; may be readily crystallized in regular octahedra; is unalterable in the air at ordinary temperatures, but when heated strongly in the presence of air, burns, emitting the yellowish-brown fumes of cadmium oxide, CdO.

**COMPOUNDS WITH OXYGEN.**—Cadmium forms a single oxide, CdO, a yellowish-brown powder, which is easily volatilized, or may be readily reduced with hydrogen or carbon, at a high temperature, but below that point necessary for the reduction or volatilization of zinc oxide. It is strongly basic and forms a series of salts similar in constitution to those formed by the oxide of zinc. It may be formed by burning the metal in the air, or by calcining the nitrate or carbonate, dif-

fering somewhat in shade according to the manner of preparation.

**ACTION OF ACIDS ON CADMIUM.**—In hot **sulphuric** or **hydrochloric acid,** moderately diluted, it is slowly dissolved, forming the salts $CdSO_4$, or $CdCl_2$, and liberating hydrogen.

In **Nitric acid** it is readily soluble, forming the nitrate, and generating nitrogen oxides.

**COMPOUNDS OF CADMIUM.**—The most important of these is the **sulphate,** $CdSO_4$, which is used in medicine as an astringent and stimulating remedy, especially in diseases of the eye. The next of importance is the *sulphide,* CdS, which occurs native as greenockite, and is used as a superior yellow pigment by artists. The *iodide,* $CdI_2$, is used in photography.

**ALLOYS.**—The metal is of little use except as a constituent of certain alloys, especially those fusing at a low temperature.

With **mercury** cadmium combines to form a silver-white mass, which readily crystallizes, and under certain circumstances is said to be malleable. When introduced into a dental-amalgam alloy, it imparts the property of malleability. Such dental alloys, however, can not be too strongly condemned.

"In 1848, Dr. Thomas W. Evans of Paris introduced his amalgam, which was composed of pure tin, cadmium and mercury; but it was soon found that cadmium was one of the very worst metals that could be used in a dental alloy, and its use was soon discontinued."*

Of it Dr. J. Foster Flagg, Philadelphia, says: "The

*Relative Merits of Filling-materials, by E. T. Darby, M.D., D.D.S., Dental Cosmos, xxxvi, p. 178.

*promises* of this alloy were certainly alluring. It was easily amalgamated; the amalgam was readily inserted; it did not discolor; it 'set' with surprising celerity; it made a sufficiently resisting filling. What wonder, then, that the gentleman who introduced it was pleased with the material! * * * My satisfaction was, however, very short-lived, for only three or four months passed before sundry indications presented, which aroused my suspicions as to the uniform integrity and durability of the material—these were, an occasional, but evident crevicing at edges; a gradual softening and disintegration of some fillings; and the yellowish discoloration sometimes apparent in adjoining tooth structure." He further states that in some cases the "dentine had become thoroughly decalcified, and stained to a bright orange-yellow color—sulphide of cadmium." He explains that pulps under such fillings were "devitalized," except "where thick septa of dentine existed between the bottoms of the cavities of decay and the pulp cavities."*

"Cadmium shares with bismuth the property of greatly reducing the melting points of alloys, there being some whose melting points are so low that they may be liquefied in hot water. But while bismuth alloys are nearly all brittle, many alloys of cadmium possess considerable ductility, and may be worked under the hammer as well as between rolls. They act, however, very differently in this respect, there being alloys which are ductile, and others again, though containing besides cadmium the same metals, only in different proportions, which are very brittle."†

*Plastics and Plastic Fillings, p. 54, First Edition.
†Metallic Alloys, Brannt, p. 297.

These alloys are usually made up of cadmium, tin, lead, bismuth, and sometimes mercury, the latter being added chiefly to lower the melting point still more. The following are a few cadmium alloys with their melting points:

| Observer or Special name* | Lead | Tin | Bismuth | CADMIUM | Fusing point C. |
|---|---|---|---|---|---|
| Lipowitz ..... | 26.70 | 13.30 | 50.00 | 10.00 | 60-68. |
| Wood ..... | 28.60 | 14.30 | 50.00 | 7.10 | 70. |
| V. Hauer ..... | 34.38 | 9.37 | 50.00 | 6.25 | 76.5 |
| Wood ..... | 42.86 | .... | 50.00 | 7.14 | 82.0 |
| ——— ..... | 33.33 | .... | 50.00 | 16.67 | 89.5 |
| V. Hauer ..... | 28.00 | 47.00 | .... | 25.00 | 132. |
| Rudberg ..... | .... | .... | 78.80 | 21.20 | 146.3 |

*Van Nostrand's Chem. Annual, 1909.

**TESTS FOR CADMIUM IN SOLUTION.—Sulphuretted hydrogen** throws down the orange-yellow sulphide, CdS, from acid solutions, distinguishing the metal from zinc.

The **Caustic Alkalies** precipitate the white hydrated oxide, Cd2HO, soluble in excess of ammonia, but insoluble in potassa or soda.

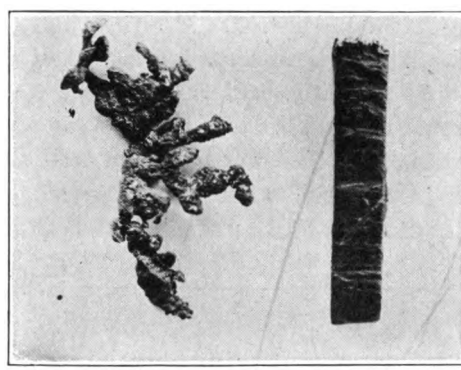
# CHAPTER XII

## COPPER

| | |
|---|---|
| Cuprum. | Symbol, Cu. |
| Valence, II ($Cu_2$) II. | Specific gravity, 8.91-8.96. |
| Atomic weight, 63.57. | |
| Melting point, 1084° C. (1065° in air) | Malleability, 3d rank. Tenacity, 2d rank. |
| Ductility, 4th rank. | Chief ore, copper pyrites. |
| Conductivity (heat), 71.98. | Conductivity (electricity), 97.6. |
| (Silver being 100.) | |
| Specific heat, 0.0936 | Crystals, isometric. |
| Color, red. | |

**OCCURRENCE.**—This exceedingly interesting and useful metal has been known and used by the human race since the most remote periods. Its alloy of tin-bronze was the first metallic compound used by man. The Smithsonian report (1868) mentions the use of native copper by the aborigines of North America, who obtained it from the southern shores of Lake Superior. Only the early inhabitants of Mexico and southern United States knew how to make bronze. It is found in the metallic state, in masses of irregular form, in rocky fissures; and often crystallized in the Lake Superior region known as Lake copper and in Virginia, the southwestern portion of the United States, in Mexico, Chile, Cornwall, and many other parts of the world. Native copper is obtained in pieces of monstrous weight on the shores of Lake Superior, many times weighing from 100 to 200 tons. The principal ores are, how-

ever, (1) *chalcopyrite,* copper pyrites, a sulphide of copper and iron, $CuFeS_2$, which when pure contains 34.6 per cent copper; (2) *Cuprite,* the red oxide, $Cu_2O$; (3)



*A* *B.*

Fig. 41.—Specimens of native copper from Lake Superior district. *A* is a crystallized mass of irregular form while *B* is a shaving produced by cutting a large mass into smaller masses by means of a sledge hammer and long-cold chisel. The reverse side is smooth while the obverse side shows the condensing effect of repeated blows of the hammer.

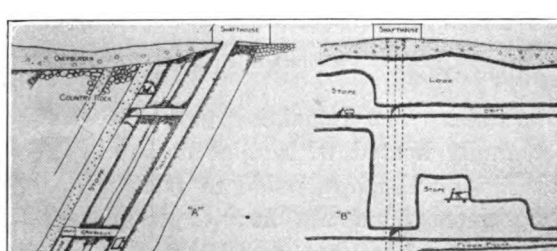


Fig. 42.—A vertical section of a copper mine in the Lake Superior district showing the method of driving the shafts and stoping along the lode.

*melaconite,* the black oxide, CuO; (4) *malachite,* green carbonate, $CuCO_3$, Cu2HO, and (5) *chalcocite,* copper-glance, the sulphide $Cu_2S$.

**REDUCTION.**—This metal is obtained from its ores by three different methods, the dry, humid, and electro-metallurgic. The process, of course, varies according to the nature of the ores treated and local circumstances.

The **dry method** is ordinary smelting, and is used for ores containing not less than 4 per cent of the metal, the wet method being preferred for the poorer ores. In the former method the ore is roasted in a reverberatory furnace, by which much of the iron sulphide is converted into oxide, while the copper sulphide remains unaltered, and any arsenic that may be present

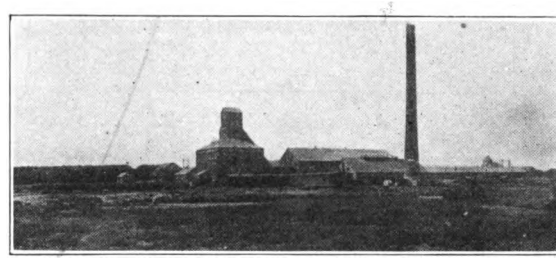


Fig. 43.—The Calumet and Hecla mine has been one of the largest and best producers of copper the world has ever known and has only been eclipsed in recent years by the mines in Utah and Montana.

is volatilized. The remaining sulphide of copper is now strongly heated with siliceous sand. The latter combines with the iron oxide to form a fusible slag, and separates from the heavier copper compound. When the iron has by a repetition of these processes been got rid of, the copper sulphide begins to decompose in the flame-furnace, losing its sulphur and absorbing oxygen, becoming an oxide, which is further reduced by greater heat and carbonaceous matter. The carbonates and oxides are reduced in much

the same manner, the former being heated to drive off the $CO_2$, thereby reducing it to an oxide, which, with the latter, is further reduced by the aid of a raised temperature and added carbon.

The **wet method**, which, as previously hinted, is desirable for ores too poor to yield a profitable quantity by the dry method. This method is frequently employed in working over what is technically known as "*blue billy*," or burnt pyrites, which remains as a residue in the manufacture of sulphuric acid from iron pyrites. Mixed with rock-salt and calcined, the small amount of copper contained in the iron oxide residue is converted into soluble cupric chloride, $CuCl_2$, and on lixiviating the calcined mass with water a solution is obtained from which the copper may be thrown down in the metallic state by scrap-iron.

**Pure Copper.**—The **electrolytic method** is used very extensively, as it yields a purer quality of the metal, which is much in demand in electrical engineering. The cathode is a thin sheet of pure copper, the anode a bar or pig of impure copper, and the bath an acid solution of copper sulphate. The pure copper is precipitated on the cathode in a highly crystalline form; the other base metals are not precipitated, but held in the acid solution, while the silver and gold are deposited in the slime and subsequently recovered.

**Commercial Copper** is quite pure, yet it frequently contains a small percentage of base metals and silver. Arsenic and antimony very materially injure the working properties of copper, while tin, producing a bronze, increases its tenacity and hardness. The impurities are of three classes:

1. Those which depress conductivity, as arsenic and antimony.

2. Those which impair ductility, as lead bismuth, tellurium.

3. Those which have a reclaiming value, as gold, silver, platinum and palladium.

**PROPERTIES.**—Copper, or cuprum, in name is derived from **kupros,** the Greek spelling of Cyprus, an island where it was extensively mined. Its symbol is the planet Venus, as the isle of Cyprus was sacred to that goddess. It is a peculiar red-colored, brilliant metal, differing in this respect from all other metallic elements, except, perhaps, titanium. Its atomic weight is 63.5, and its specific gravity, 8.91. It takes a brilliant polish, and is very malleable and ductile, being second to iron in point of tenacity. It may be rolled into thin sheets or drawn into very fine wire. A copper wire, hard drawn, having a sectional area of a square millimeter, sustained a weight of 90.20 pounds at the moment of rupture. The same wire, annealed, broke under a weight of 69.52 pounds.* The melting point of copper is probably best stated at 1084°-1065° in air, and it expands slightly on passing from the molten to the solid state. It is unaffected by dry air, but in a moist atmosphere it becomes coated with a green carbonate, **malachite,** which is also found native in most beautiful shades, takes a high polish, and is used for ornamental articles. When heated or rubbed with much friction, it emits a peculiar, disagreeable odor. In the conductivity of heat (71.9) and electricity (97.6) it is second only to silver (100).

*Gannot, Elements de Physique.

**DENTAL APPLICATIONS.**—Metallic copper has long been used for various purposes in the mouth, and was formerly used in the form of an attenuated, cone-shaped point known as canal points, for filling pulp canals, accompanied with a coating of some plastic-filling substance, such as chloropercha. Very thin sheet copper is cut into narrow strips about an inch and one-half long, and used for obtaining the circumferential measurement of teeth or roots before crowning. Copper bands of the same gauge and diameter as seamless gold shells are now furnished for the convenience of the operator, thus saving much time. These bands are also adapted to broken down teeth in the mouth, for introducing large contour amalgam fillings, thus lessening the danger of fracturing the amalgam during the setting stage.

Dr. Charles B. Atkinson recommends swaging copper plate as retaining caps secured by copper wire in the treatment of pyorrhea alveolaris.* It is further used as concave disks for the protection of exposed pulps, and the wire as a ligature for retaining the rubber-dam in position.

The foil in the form of pellets or ropes has been used as a filling material, inserted beneath gold surfaces; also to finish off the amalgam fillings, absorbing the surplus mercury.

Copper pans are used for subjecting gold bases during the course of construction to the action of boiling dilute sulphuric acid.

**Copper poisoning** shows a red, or purple-red *or "sometimes greenish-brown"* (Hirt), line near the margin of the gums, says Professor W. D. Miller, and further,

*Dental Cosmos, xxxii, p. 549.

teeth of copper workers * * * show a more or less pronounced greenish discoloration. * * * Teeth filled with copper amalgam often show a greenish surface discoloration.*

**COMPOUNDS WITH OXYGEN.**—Copper forms two oxides of importance, each of which is found native:

**Copper monoxide,** *Cupric oxide* or *Black oxide,* CuO, is prepared by calcining metallic copper at a red heat in the presence of air, or by heating the nitrate to redness, driving off the $NO_2$. It forms a series of very important blue and green cupric salts, isomorphous with the salts of magnesium. It imparts a green color to glass, and is much used in the chemical laboratory as a means of supplying oxygen for the combustion of organic substances. When a caustic alkali is added to a cupric salt, a light blue precipitate, hydrated copper oxide, Cu2HO, is formed, which, if heated to 100° C., loses its water of crystallization and falls as a black oxide. This oxide is soluble in acids.

**Cuprous oxide,** *Red Oxide* $Cu_2O$, occurs, in nature as a ruby-red octahedral crystal. It may be prepared by heating in a covered crucible 5 parts of the black oxide and 4 parts of fine copper filings. It gives to glass a beautiful ruby-red color.

The most important cuprous salt is the chloride, CuCl, a white solid obtained by dissolving a mixture of cupric oxide and metallic copper in hydrochloric acid. It possesses a remarkable property of absorbing carbon dioxide.

**ACTION OF ACIDS ON COPPER.**—Copper does not dissolve in acids with evolution of hydrogen.

In **nitric acid** it dissolves most readily, chiefly with the evolution of nitric oxides—

*Dental Cosmos, xxxvi, p. 265.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO,$$

and forms copper nitrate.

In **sulphuric acid,** hot and concentrated, it also dissolves readily, with evolution of sulphurous anhydride—

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2$$

and forms copper sulphate—blue vitriol.

In **hydrochloric acid** copper is slowly soluble.

**EXPERIMENT No. 53.**—In test tubes containing each of the above acids drop small strips of copper plate; heat and note reaction.

**ALLOYS.**—The preparation of copper alloys is generally attended with many difficulties, on account of the high fusing point of the metal and the almost invariable presence of small quantities of other elements. An analysis of electrolytic copper having a conductivity of 100% showed the presence of the following elements:

| | |
|---|---|
| Cu | 99.93 |
| Ag | .001 |
| Au | .00001 |
| S | .003 |
| O | .04 |
| Fe | .0035 |
| Ni | .004 |
| As | .002 |
| Sb | .003 |
| Al | .001 |
| P. | trace |
| Pb | .002 |
| Bi | trace |
| Si | .0005 |
| Te | .0005 |
| | 99.99051 |

Copper must always be protected from oxidation in fusing for the cupric oxide formed tends to dissolve in the melted metal and make it springy.

**Mercury** with copper readily forms an amalgam of definite chemical proportions, having the formula CuHg. It crystallizes easily and, on solidifying becomes very hard and takes a fine polish. It is also malleable, and can be worked under the hammer and between the rollers. It retains its metallic luster though for some time exposed to air, but blackens quickly when in contact with air containing sulphuretted hydrogen. It may be softened by heat, and is again plastic and flexible, solidifying subsequently.

These peculiar properties, together with others, led to its introduction as a binary dental amalgam, first known as *Sullivan's Amalgam* or *Cement.**

**Gold** and copper alloy readily, the latter giving a desirable hardness to gold and deepening its color. If, however, any considerable proportion of copper be added to gold, the alloy is apt to be brittle, especially if the copper be not absolutely pure. For United States gold coins 10 per cent of copper is added to pure gold, giving it a carat fineness of 21.6, and a proper degree of hardness for durability.

**Silver** and copper also alloy readily, and the copper again gives hardness with a slight change of color. Ten per cent of copper is added to silver for United States coin.

**Platinum** and copper alloy at an intense white heat, giving an alloy much resembling gold in color and specific gravity.

*See chapter on Amalgams, p. 355.

**Lead** added to copper from .001 to .003 somewhat increases its ductility and malleability, but the presence of 0.001 renders the metal unfit for preparation of malleable or ductile brass.

**Iron** to the amount of .003 also has an injurious effect upon the properties of copper, rendering it hard and brittle.

**Antimony, bismuth** and **arsenic** in small quantities have a very injurious effect upon copper.

**Zinc** alloys with copper in any proportion, all the alloys of which are included under the term *brass*. Alloys of copper and zinc were known in the time of Aristotle, and the manufacture of brass was first introduced in Germany in 1550, but was probably not produced by the direct union of the two metals until 1781 in England, as the art of obtaining zinc in the metallic form became known but a short time previous to that period. Notwithstanding copper and zinc may be alloyed in any proportion, the product is always serviceable. "Generally speaking, it may be said that with an increase in the percentage of copper the color inclines more toward a golden, the malleability and softness of the alloy increasing at the same time. With an increase in the percentage of zinc, the color becomes lighter and lighter, and finally shades into a grayish-white, while the alloy becomes more fusible and brittle and at the same time harder."* Alloys containing from 15 to 20 per cent zinc are the most ductile. Those of 36 to 40 of zinc can be worked cold as well as hot, while those containing 60 to 70 of zinc are so brittle that they can not be worked at all. Raising this percentage to

*Brannt, Metallic Alloys.

from 70 to 90 of zinc, the alloy again becomes ductile, and can be worked quite well when hot, but not when cold. An alloy of copper 75 and zinc 25 fuses at 960° C.

When cupric oxide is heated with powdered zinc in equal proportions, zinc oxide is formed and copper is freed. When zinc oxide and copper are heated to the melting point of copper, there is no loss of weight of copper. Therefore the oxide in brass is presumably zinc oxide. It is not dissolved in brass and therefore must be mechanically entangled.

**Good sheet brass** may be made according to many formulæ; two are cited:

Rosthorn (Vienna)—Copper 68.1 and zinc 31.9 parts.
Romilly—Copper 70.1, zinc 29.26, lead 0.38, and tin 0.17 parts.

**For wire,** the following:

England—Copper 70.29, zinc 29.26, lead 0.28, and tin 0.17 parts.
Neustadt—Copper 71.5 and zinc 28.5 parts.*

Alloys containing as high as 37 per cent of zinc are used as ductile and malleable products.

The brass trade classes brass as (1) high brass, (2) low brass, (3) Muntz metal, (4) gilding, and (5) bronze. High brass is the most extensively used, and is known as "common brass." It carries from 61 to 70 per cent of copper, the remainder being zinc. Spinning brass, cartridge brass, dipping brass, and screw rod brass are all high brass, although the last mentioned contains some lead to allow it to cut freely. Low brass is softer and has more stretch. It is used for drawing and spinning, and for brazing. It carries from 75 to 80 per cent of

*Figures from Brannt, Metallic Alloys.

copper, the rest being zinc, and the color is usually a greenish yellow. All brasses carrying over 40 per cent zinc are known as Muntz metal. They will roll hot and are used for the cheaper grades of brass products. Gilding is a gold-colored mixture of copper 90, and zinc 10, used in cheap imitation jewelry. Bronze consists of this gilding alloy with some tin, usually, Cu 90, Zn 9, Sn 1, and is the best formula for rolling.

**Fine cast brass** usually contains from 20 to 50 parts of zinc to 100 parts copper, together with lead, or tin, or both in the proportion of 0.25 to 3 per cent of each.*

**Gun metal** is classed as a brass alloy. For work requiring the highest tensile strength, (30,000 lbs. per square inch) the formula is Cu 88, Sn 10, Zn 2. For free turning gun metal the formula is Cu 86, Sn 10, Zn 2, Pb 2. It casts exceptionally well with a small amount of shrinkage, is stiff, strong and noncorrosive.

"The most malleable of the brasses is *Dutch metal*, composed of copper 11, zinc 2 parts; it can be rolled out into thin sheets and afterward beaten into leaves of extreme tenuity, and is used in this form for decorative purposes under the name of *Dutch leaf-gold*, or reduced to powder by levigation with a small quantity of oil or honey, it is sold as bronze powder."†

**Pinchbeck**, an alloy of copper 88.8 and zinc 11.2 parts, very much resembles gold; is very ductile and malleable; used for cheap jewelry.

**Mosaic gold**, a term sometimes applied to tin sulphide, is composed of about equal parts of copper and zinc.

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*Figures from Brannt, Metallic Alloys.
†Kirk, American System of Dentistry.

**Copper coins.**—Those of the United States are composed of copper 95, tin 3, zinc 2 parts.

**Nickel** and copper unite in all proportions, the color varying from the red of copper to the blue-white of nickel, according to the proportions of the respective metals.

Copper with 10 per cent of nickel gives a light copper-colored alloy, very ductile; with 15, the color is a very pale red, but the alloy is still quite ductile; with 25, a nearly white alloy, and 30, a silver-white alloy. United States nickel coins are composed of copper 75, and nickel 25 parts.

**Nickel, copper** and **zinc** alloys are called **German silver, argentan,** etc. They are in reality brasses with nickel added, which gives them a white color and much hardness.

These compositions vary greatly as may be noticed:

| | |
|---|---|
| Copper | 50 to 66 parts |
| Zinc | 19 " 30 " |
| Nickel | 13 " 18 " * |

**White metal.**—A variety of alloys consisting of copper and a large proportion of zinc. They are very white, or, depending upon the proportion of copper, may be a pale yellow; melt at a low point, may be cast, and are somewhat malleable and ductile.

**Aluminum** alloys easily with copper, producing aluminum bronze, the alloys showing different properties, according to the quantity of aluminum they may contain. It makes copper harder and tougher without affecting its ductility, but renders it more liable to absorb

*Brannt, Metallic Alloys.

oxygen. With 60 to 70 per cent aluminum, a very brittle alloy is produced; with 50 per cent, one quite soft, but less than 30 per cent of aluminum, the hardness returns. The bronze composed of copper 95, aluminum 5, is a beautiful gold color, takes a fine polish, casts well, is malleable hot or cold, and is very strong, especially after hammering. With 7.5 per cent aluminum, the color is a greenish golden. The most common alloy is 10 per cent aluminum, having a bright golden color which is not tarnished in air, may be engraved, possesses, it is said, greater elasticity than steel, and may be soldered with 20-carat gold solder. It melts at about 927° C.

**Tin** and copper form a very important series of alloys termed bronze. (See chapter on Tin.)

**Brazier's Solder.**—An alloy composed of copper, zinc, tin and lead in variety of proportions, according to color and fusibility.

Dr. Kirk gives the following table:

| | Copper | Zinc | Tin | Lead |
|---|---|---|---|---|
| A. Golden Yellow..... | 53.50 | 43.33 | 2.12 | .... |
| B. Medium light..... | 43.75 | 50.58 | 3.75 | 1 |
| C. White ..... | 57.50 | 27.90 | 14.90 | trace |

It is used in soldering brass and copper, which may also be soldered with the ordinary soft solder, spelter (zinc), or silver solder.

**Solders.**—Copper is a constituent of most hard solders; its proportion varying according to the purpose for which they are to be used. (See chapters on Silver and Gold.)

**DENTAL-AMALGAM ALLOYS.**—Copper is a valuable ingredient in these alloys, and is generally used in a proportion varying from 1 to 8 per cent. (See Amalgams.)

**TESTS FOR COPPER IN SOLUTION.—Sulphuretted hydrogen** added to either acid, alkaline, or neutral solutions of copper throws down a brownish-black precipitate of cupric sulphide, insoluble in dilute acids or alkalies, but soluble in potassic cyanide.

**Potassium** or **sodium hydrate** throws down a light blue cupric hydrate, Cu2HO, insoluble in excess of either reagent, but, if heated, falls as the black cupric oxyhydrate, ($CuO_2$) Cu2HO.

**Ammonia,** or its carbonate, gives a blue precipitate, soluble in excess, producing a deep blue solution.

**Potassium ferrocyanide** yields a characteristic brown precipitate, soluble in ammonia and decomposed by potassa.

**Metallic iron** placed in a solution containing copper precipitates the latter upon itself in the metallic state. Zinc or tin precipitates it as a black powder.

**ELECTRODEPOSITION OF COPPER.**—Copper may be deposited by simple immersion from a sulphate solution. The same solution is used for coating all metals and alloys, such as brass and German silver; but zinc, iron, lead, steel, tin, Britannia metal, type metal, etc., which precipitate it from its solutions by simple immersions, are coated in the cyanide or other alkaline solutions. Fruits, flowers, insects, etc., may be coated with a film of copper from the sulphate solution and a single cell.

**Plaster casts** of the mouth are easily coated by first boiling in wax and coating when cold with plumbago and tin bronze.

# CHAPTER XIII

## IRON

| | |
|---|---|
| Ferrum. | Symbol, Fe. |
| Valence, II, IV ($Fe_2$)IV VI. | Specific gravity, pure 7.85-7.88. |
| Atomic weight, 55.84. | Malleability, 9th rank. |
| Melting point, pure 1505° C. | Tenacity, 1st rank. |
| Ductility, 5th rank. | |
| Conductivity (heat), 16.65. | Conductivity (electricity), 14.6. |
| (Silver being 100.) | |
| Specific heat, 0.1162. | Chief ores, hematite, magnetite, and siderite. |
| Color, grayish-white. | Crystals, cubical. |

**OCCURRENCE.—Iron** is widely and abundantly distributed throughout nature, being found in nearly all forms of rock, clay, sand and earth; its presence in these being commonly indicated by their colors, for iron is the commonest of all natural mineral coloring ingredients.

*Meteoric Iron*—Metallic iron is very rarely found in nature, nearly all of which is probably of meteoric origin, with the exception of ferruginous metallic platinum. True meteoric iron usually, if not invariably, contains nickel to the extent of 1 or 2 per cent.

**Ores of Iron.**—The chief combinations in which iron is found in sufficient quantity to render them available sources of the metal are shown in the table* on page 210.

*Magnetic Iron*—Magnetite, or loadstone, $Fe_3O_4$, is found massive in very large quantities in Norway, United States, Canada, New Zealand, and India. The

*Bloxam's Chemistry Inorganic and Organic, p. 332.

| Common Name | Chemical Name | Composition |
|---|---|---|
| Magnetic iron ore. | Protosesquioxide of Iron... | $Fe_3O_4$. |
| Red hematite..... | Sesquioxide of Iron..... | $Fe_2O_3$. |
| Specular iron..... | Sesquioxide of Iron..... | $Fe_2O_3$. |
| Brown hematite... | Hydrated sesquioxide of Iron | $2Fe_2O_3.3H_2O$. |
| Spathic iron ore.. | Carbonate of Iron..... | $FeO.CO_2$. |
| Clay iron-stone... | Carbonate of Iron, with clay | ..... |
| Blackband ..... | Carbonate of Iron, with clay and bituminous matter... | ..... |
| Iron pyrites..... | Bisulphide of Iron..... | $FeS_2$. |

ore of Norway furnishes the Swedish iron of such excellent quality, and the sands of New Zealand and India the excellent Wootz steel. It contains, when pure, about 72 per cent of iron.

*Red hematite,* $Fe_2O_3$, is found in abundance in England, occurring in hard, shining, rounded masses of a dark red-brown color. It is a very characteristic ore of iron, containing from 47 to 70 per cent of the metal.

*Specular Iron,* like red hematite, is an anhydrous sesquioxide ($Fe_2O_3$), but differs greatly in appearance, being of a steel-gray color and brilliant luster. It occurs chiefly on the island of Elba, but is also found in Germany, France, and Russia. The excellent quality of iron obtained from this is probably due to the purity of the ore, and to the fact that charcoal, instead of coal, is employed in smelting it. It contains about 62 per cent of iron. *Red ochre* is a soft variety of this ore, containing clay.

*Brown Hematite,* limonite, $2Fe_2O_3.3H_2O$, is the hydrated sesquioxide. It is of a distinctly sedimentary character, forming beds, but is also found in veins. It occurs principally in Belgium and France, and contains

about 15 per cent water, and, when pure, about 59 per cent iron. *Yellow ochre* is a variety of this ore.

*Spathic ore,* siderite, ferrous carbonate, $FeO.CO_2$, or $FeCO_3$. The value of this ore depends as much upon the nature of its impurities as upon the percentage of iron. It is found in Saxony of a crystalline character, light brown or gray in color, having a pearly luster, and when pure contains about 48 per cent iron.

*Iron pyrites,* $FeS_2$, is particularly remarkable for its yellow color, brilliant metallic luster, and crystalline structure, from which facts it has been termed "fools gold." It does not form a direct source of iron, but the residue left after burning pyrites to make sulphuric acid, and extracting the copper,* is almost entirely of ferric oxide, from which iron is ultimately reduced.

**REDUCTION.**—If the ore is a carbonate, or contains any carbonate, it is usually first calcined to expel the water and carbon dioxide, by roasting in a kiln or in long pyramidal heaps, resting upon foundations of large lumps of coal. This process reduces the ore to a dry, porous mass, and the iron to an oxide. Much of the sulphur, nearly always present, is driven off as sulphur dioxide at the same time.

The calcined ore is then mixed with a certain proportion of limestone (calcium carbonate) as a flux, which is to induce the earthy part of the ore to flow, in order to liberate the iron. With the proper quantity of coal, coke, or charcoal, it is then introduced into one of the great blast-furnaces.†

It would be very easy to reduce the oxide contained

*See chapter on Copper.

†See chapter on Melting Metals.

in the calcined ore to metallic iron in such a furnace when heated with carbon; but the metallic iron fuses

Fig. 44.—A crude type of blast furnace used by the native Filipinos for the reduction of iron. The principles involved are much the same as are used in the modern blast furnace.

with so great difficulty that it is impossible to separate it from the clay, unless the latter is brought to a liquid

state, and even then the fusion of the iron, which is necessary for complete separation, is only effected after

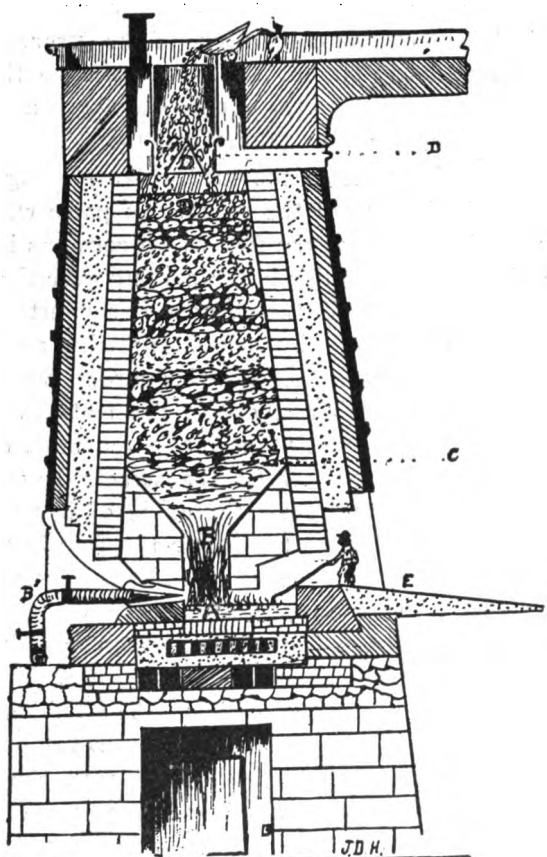



Fig. 45.—Sectional view of blast furnace.

it has formed a more easily fusible compound with the small proportion of carbon derived from the fuel. The

clay is even more difficult to fuse than the iron, so it is necessary to add with the ore to be smelted some substance capable of forming with clay a combination which is fusible at the temperature of the furnace. As has been previously stated, limestone produces the required result by forming the double silicate of alumina and lime, which becomes perfectly fluid.

As the air passes from the tuyère (at *B'*, Fig. 45) pipes into the bottom of the furnace, it parts with its oxygen to the carbon of the fuel which converts it into carbon dioxide ($CO_2$); this latter passing over the red-hot fuel as it ascends in the furnace is converted into carbon monoxide (CO) by combining with an additional quantity of carbon. It is this carbon monoxide which reduces the calcined ore to the metallic state, when it comes in contact with it, at a red heat, in the upper part of the furnace, for this abstracts the oxygen at a high temperature, from the oxide of iron; itself becoming carbon dioxide, the iron remaining in a free state. The tendency in the past has been to select the flux or limerock carefully, to wash the coal, or screen the coke and pick the iron ore and then introduce a blast of air containing four-fifths nitrogen which robs the furnace of a great deal of heat. The tendency in the future will be to manufacture cheap oxygen at the plant or employ air rich in oxygen to save heat and fuel. In determining the weight of gases passing out of the stack, it was found that they amount to twenty times the weight of the slag. The metal as it melts being the heavier sinks by its own gravity through the fuel into a crucible or cavity (*A*, Fig. 45) at the bottom of the furnace; as it sinks, however, it combines with small proportion of carbon to form cast

iron. At the same time the fluid slag, composed of the clay, or earth, made fluid by the addition of carbonate of lime as a flux, sinks also into the crucible, built at the bottom of the furnace, where it forms a layer of slag over the molten metal. When the slag so accumulates that no more will be contained in the crucible, it is allowed to run over its edge down the incline (*E* in Fig. 45) on which the furnace is built. Thus the process is carried on until there is sufficient metal melted to constitute what is termed a charge, which rises almost to the aperture of the blast. The furnace is then tapped, at an opening provided for that purpose, and the metal run off into molds, when it is cast into rough, semi-cylindrical masses called *pigs*—crude cast iron. For purposes where hardness without flexibility is wanted, the remelted iron in this state is extensively used.

**ELECTRIC FURNACE REDUCTION.**—The process of reduction in the electric furnace is a modification of the blast furnace method. The furnace is usually of a smaller type, the one at Heroult, Cal., being a rectangular steel box 27 feet long, 13 feet wide, and 12 feet high, lined with fire brick. Four graphite electrodes supply the current at from 40 to 80 volts. No air is allowed to enter, as in the blast furnace and the carbon used is only for purposes of reduction. A charge consisting of 500 lbs. of magnetite ore, 140 lbs. of charcoal, 3.5 lbs. of lime, 12.5 lbs. of quartz is fed into the furnace at stated intervals. The furnace is tapped three times a day and from six to seven tons of high grade pig iron is run off each time. The cost approximates $14 a ton.

The electric furnace offers a particularly favorable means of working over steel scrap. It is possible to

melt nickel, chrome, or vanadium steel, old tools, etc., make an assay of the product, add the necessary elements and produce a good steel alloy. The quality of castings made in the electric furnace, especially for automobiles, is considered superior to that made by any other process.

**PROPERTIES.**—Pure iron is a hard, malleable, ductile and tenacious metal, of a grayish-white color, and of fibrous texture, a slightly styptic taste, and has a sensible odor when rubbed. Its strength and tenacity are very high. In magnetic character it is superior to all other substances, nickel and cobalt being next. When it is almost pure, the magnetic influence produced, owing to induction, by the proximity of a permanent magnet or of an electric current, disappears entirely on removal of the magnet or current; if, on the other hand, carbon be present (as is usually the case to some small extent even in the softest malleable iron), there remains, after the removal of the magnet, or current, a greater or less amount of permanent magnetism, according to the circumstances; hard steel exhibiting the greatest power of becoming permanently magnetized under given conditions. In thermic and electric conductivity iron is 16.65 and 14.6 respectively. Its specific gravity is 7.85, its specific heat 0.1162, and its melting point is variously estimated from 1500°-1600° C. (Pouillet) to 1900°-2000° C. (Deville). The presence of minute quantities of carbon, sulphur, etc., very sensibly lowers the fusing point, while 1 per cent of the former furnishes a steel melting at several hundred degrees lower than pure iron. Cast iron, containing more carbon, melts very much lower. It possesses the remarkable prop-

erty of becoming plastic just before fusion, so that two hot masses may be pressed or squeezed together into one by the process of *welding*. So by forging, rolling, hammering, or other analogous operations, it can readily be fashioned into shapes which its rigidity and strength when cold will enable it to maintain. It is combustible and, when heated to whiteness, burns in atmospheric air, and with brilliant scintillations in oxygen gas. It combines with all the nonmetallic elements, except hydrogen and nitrogen, and with most of the metals.

**MODIFICATIONS OF IRON.**—There are three distinct modifications of iron, viz., **cast iron, wrought iron and steel.** Other immediate varieties are recognized technically, but all are closely related and imperceptibly shaded into each other, due to various percentages of carbon, etc., contained in the metal. The discovery that carbon in varying proportions with iron constitutes steel and other classes of iron dates from about 1790 and probably emanates from England.

**CAST IRON** is an impure carburized iron. The melted metal drawn off from the furnace below is conducted into a large main, called the *"sow;"* and thence into lateral molds called *"pigs;"* hence the term pig iron. This iron is found to have combined with a considerable quantity of carbon, about 4.5 per cent being the maximum; a portion of which exists as a chemical combination, the carbide of iron, the remainder having been simply dissolved in the form of graphite. Other substances in the furnace are also found dissolved and combined in the iron, and have an important bearing upon its physical properties. These

are principally phosphorus, silicon, sulphur, manganese, etc.

*Pig iron* may, therefore, be recognized as a crude form of cast iron. It is assorted and classed by the iron masters as Nos. 1, 2 and 3, differing in the amount of carbon contained. No. 1 is most highly carburized, No. 2 less, and No. 3 contains the least carbon. The first melts and runs so fluid that it is used for ornamental castings of fine pattern, and furnishes cast-iron cutlery from which the carbon is subsequently extracted.

Cast iron, which contains the most carbon, is the most fusible variety, melting at about 1200° C. It is hard and brittle. Though some kinds admit of being made hard or soft nearly in the same manner as steel, and like steel, assume different degrees of hardness, according to the rapidity with which the pieces are allowed to cool; but unlike steel, when once hardened, will not admit of that hardness being reduced by various gradations to any specific degree, called tempering. To soften materially it must be submitted for some time to a white heat, and then very gradually cooled.

**WROUGHT IRON** is the cast, or pig iron, freed from carbon, and may be considered a nearly pure decarburized iron; at least, it is the purest form of commercial iron, containing the least amount of carbon—less than 0.25 per cent. The decarburization is effected by first remelting the pig, or cast iron, and refining by exposing it to an intense heat and forcing a blast of air over its surface, in order to remove some of the impurities of the metal; it is then run out into a large flat mold, and acquires the name of *plate metal*.

The next process is called "*puddling,*" the object being to free the metal of its carbon. The operation is conducted in a reverberatory furnace, where the metal is again reheated and converted into wrought iron by keeping it in a state of fusion with a certain amount of black oxide of iron, $Fe_3O_4$, which gives up its oxygen after a time to the carbon and other impurities of the melted mass, leaving the latter nearly pure iron. As the process approaches termination, the fusing point of the mass grows higher, until it loses nearly all its fluidity. It is then divided into several parts and formed into balls, which are removed from the furnace and subjected to intense pressure through a series of powerful rollers, which squeeze out the more fusible slag entangled in it and convert it into bars or "*blooms.*" A number of these blooms are then raised to a welding heat and repeatedly passed through rollers, until all the remaining slag is forced out and the metal becomes tough and fibrous. Thus the process is repeated, usually once, and sometimes—to produce a superior iron—twice or three times. By this process the metal is converted from a fusible, hard and brittle substance, as cast iron, into a tough, elastic *bar;* in fact, it has been rendered malleable, ductile, more closely compact, and of a fibrous texture, and is less fusible. It is also very tenacious, and added to its properties is a new and remarkable one, by virtue of which two pieces being heated similarly may be forged or welded together. For purposes where lightness, strength, and durability are wanted, it is more extensively employed than cast iron. In this state it is known in commerce as *bar,* or *wrought iron.*

**STEEL** is composed of iron and carbon, and is sometimes formed from wrought iron, by heating the latter in contact with carbon, and sometimes from cast iron, by depriving it of impurities, and all but a small percentage of carbon. The proportion of carbon varies, of course, in the different qualities of steel; but in that used ordinarily the carbon rarely exceeds *one and one-half per cent;* for some purposes it is as low as *one per cent.* Good ordinary tool steel contains about *one and one-half per cent* of carbon.

Different kinds of iron produce steel of different properties, and different qualities of steel are used for different purposes.

To harden iron, add carbon.

To harden steel, add tungsten, nickel, or chromium.

For steel for magnets, add molybdenum.

For steel with high electrical resistance, add nickel or chromium.

For steel with good wearing qualities, add titanium.

To make steel tough, add vanadium.

There are two distinct processes employed for the production of steel, known as the **Cementation Process** and **Bessemer's Process.*** By the latter process steel can be manufactured of any degree of hardness directly from the cast iron, without the intermediate operation of making it malleable by puddling, etc. The principle of the process consists in directing a blast of cold air upon the molten cast iron contained in a *"converter."* The oxygen of the blast combines

*There are many processes for the manufacture of steel, but these two processes are typical, and, generally speaking, all processes are but modifications of either one of these two ways—i. e., by adding a certain percentage of carbon to a lightly carburized iron, such as wrought iron; or by abstracting an amount of carbon from a heavily carburized iron, such as cast iron.

with the carbon, silicon and manganese. Sulphur and phosphorus are difficult to remove by this process; hence the necessity of employing ores as free from these as possible. The intense combustion of the carbon in the iron is attended with great elevation of temperature, so that the metal is maintained in a fluid state throughout the whole operation, solely by the energy of the reaction in the converter. Thus the cast or pig iron is decarburized, or converted into tool steel, or to mild welding steel, or to the state of malleable iron, according to the length of time the combustion is continued. It has been found, however, that a better quality of steel can be produced by continuing the decarburizing and purifying process until all, or as nearly all as possible, of the carbon and impurities are removed, and then adding to the fused wrought iron a certain quantity of a peculiar kind of white cast iron known as *spiegel-eisen** "looking glass" iron, containing a known quantity of carbon and a little manganesium and silicon.

Bessemer steel is largely used in the construction of railroads, bridges, armor plates for vessels, girders, etc., in the construction of edifices, the manufacture of machinery, tools, etc.

**The Cementation Process.**—The furnace in which the iron is cemented and converted into steel, called a converting furnace, has the form of a large oven, constructed so as to form in its interior two large and long cases commonly called troughs or pots and built

*Spiegel-eisen is composed of the following:

| | |
|---|---|
| Iron | 82-86 |
| Manganesium | 10.71 |
| Silicon | 1.00 |
| Carbon | 4.32 |

of good fire-stone or fire-brick. Into each of these pots layers of the purest malleable iron bars, and layers of pulverized charcoal are packed horizontally, one upon the other, to a proper height and quantity, according to the size of the pots, leaving room every way in them for the expansion of the metal when it becomes heated. After the packing is completed, the tops are covered with a bed of sand or clay. This is to confine the carbon and exclude the atmosphere. The whole is then heated for eight or ten days, according to the degree of hardness required. Then the mass is left to cool for several days.

The properties of the iron are remarkably changed by this process; it acquires a small addition to its weight, becomes much more brittle and fusible than originally, loses much of its ductility and malleability, but gains in hardness, elasticity and sonorousness. The texture, which was fibrous before, has now become granular; and its surface is found to be covered with blisters, and it presents, when broken, a fracture much like inferior iron. Iron under this process has been shown to have taken up about 1 per cent of carbon. It is, however, far from being homogeneous in composition, and is called *blister steel.* Uniformity of composition is secured by subjecting bundles of the carburized iron bars to repeated blows from a steam hammer, at a welding heat, striking in rapid succession, until it closes the seams and removes the blisters. It is then termed *shear steel.* After this treatment is repeated, it is called *double-shear steel.* Homogeneity is best obtained, however, by using the blister steel in crucibles, covering the mass with clay or some other substance to exclude

air, and casting it into ingots. It is then designated as *cast steel* or *crucible steel.*

*Spring steel* is blister steel simply heated and rolled.

*Case hardening* is accomplished by heating such articles of forged, or bar iron, as it is desired to harden superficially in contact with some substance rich in carbon and afterwards chilling them in water. Gun-locks are thus treated.*

*Red-short.*—Sulphur when present in as small a proportion as 0.1 per cent serves to make the metal brittle and liable to fracture when worked or rolled at red heat, hence the term.

*Cold-short.*—Phosphorus, when present, renders the steel brittle when cold. It serves, however, to neutralize the effect of sulphur; but steel containing phosphorus is extremely difficult to temper.

*Harveyized steel,* which is employed for armor plate on account of its extremely hard and resistant surface, is prepared by heating the steel plate to the melting point of cast iron and then tightly packing its surface with carbon; after it has taken up about 1 per cent of the carbon, the plate is dropped into water and cooled.

**Nickel Steel.**—In 1889, M. Henry Schneider of Creusot, France, patented an alloy of steel and nickel. The alloy usually contains about 5 per cent of nickel, and is especially suitable for use in the construction of ordnance, armor-plate, gun-barrels, and projectiles. It is said that ordinary steel is more readily acted upon by sea water than are the more impure grades of iron, but

*The best temperature for case hardening is from 950° to 1000° C. This is only high enough to allow supersaturation of carbon at the surface of the steel.

nickel steel is less liable to corrode in salt water than ordinary steel.

**Chrome Steel.**—Chromium gives greater hardness, tensile strength, and elasticity to iron, but decreases its weldability. It is also stated that chromium steel is more susceptible of oxidation than ordinary steel. Chromium is added to iron by heating the mixed oxides of iron and chromium in a brasqued crucible with pulverized charcoal and fluxes. Chrome steel is then produced by melting chrome iron with wrought iron or steel in graphite crucibles.

**Manganese Steel.***—When about 15 per cent of manganese is added to steel, it produces an alloy of great strength and toughness, and so hard that it is almost impossible to work the product by ordinary methods. The alloy is usually prepared by adding manganese iron to molten Bessemer, or open-earth steel. From 4 to 5 per cent of manganese gives to the alloy its extreme brittleness. Extremes of atmosphere, heat or cold, do not appear to affect the properties of manganese steel. When a piece of it is heated sufficiently to be seen red hot in a dark room and is plunged into cold water, it becomes soft enough to be easily filed. Hardness is then restored by reheating to a bright red and cooling in air. The presence of manganese in proper proportions in nickel steel is said to very much improve it. Indeed, the best results are only obtained by the admixture.

**Copper Steel.**—This alloy usually contains from 5 to 20 per cent of copper, according to the purpose for which it is to be used. It possesses remarkable

*Manganese steel is chiefly used for safes and rails.

strength, tenacity, and malleability, and these properties are still further developed by tempering.

**Aluminum Steel.**—In amounts not greater than 1 per cent, aluminum is said to slightly increase the tensile strength and proportionally, the elastic limit, of rolled and cast steel.

**Arsenic, Antimony, Bismuth.**—Arsenic in small quantities and bismuth in slightly larger quantities, improves the magnetic qualities and increases the electrical resistance of iron. The presence of antimony always injures the mechanical strength of iron.

**Tungsten** in small quantities produces an exceedingly hard steel, without the necessity of tempering.

**CARBURIZED IRON.**—As has been previously hinted, carbon may be present in iron under two conditions. When iron is fused in contact with carbon, it is capable of combining with nearly 6 per cent of the latter element, to form a white, brilliant, and brittle compound, which may be represented pretty nearly by $Fe_4C$. Under certain circumstances, as this compound of iron and carbon cools, a portion of the carbon separates from the iron and remains disseminated throughout the mass in the form of minute crystalline particles very much resembling natural graphite.

Iron containing the least possible carbon, and otherwise comparatively pure, is called *wrought iron.*

Iron containing from 1.04 to 4.81 per cent of carbon is designated as *cast iron.*

Iron containing from 0.15 to 1.04 (Bloxam) is considered steel. "The portion of combined carbon within certain limits bears a direct relation to the tensile strength of the metal, variations as minute as .01 per

cent, making a considerable alteration in this quality. The same is true of hardness, the effect of carbon up to a certain point being to increase tenacity and decrease ductility, and also to cause the metal, when heated and suddenly cooled, to become more or less hard, the hardening being in direct proportion to the amount of carbon present and the rate of cooling."*

One and four-tenths per cent of carbon in iron produces a highly carburized steel that must be worked with great care. It should not be heated above a cherry red, for fear of burning. Such steel is used for the manufacture of razors, and tools for cutting hard metals.

Steel containing from 1 to 1.25 per cent of carbon is used for making most tools.

Steel containing about 1 per cent of carbon can be welded readily, and a portion of a tool made of it can be made tough, so as to stand a blow from a hammer, without chipping, while another part can be hardened, as in the case of a cold chisel.

**GALVANIZED IRON.**—Iron oxidizes so readily in the presence of moisture that some measures must be taken to prevent this corrosion when the metal is subjected to moist atmospheres. The common method is by galvanizing, though various pigments and hydrocarbon compounds are employed. A metallic coating to be protective must be electropositive to the underlying metal, and though copper, bismuth, tin, lead, cobalt, and nickel are such, none are so useful as zinc. The galvanic property becomes useful when the iron becomes exposed, since the current flows from

*Kirk, American System of Dentistry, iii, p. 900.

the iron to the zinc, the latter being corroded rather than the former.

There are three methods of galvanizing: (1) Hot galvanizing, or dipping the iron into molten zinc. (2) Wet galvanizing, or electroplating the zinc on the iron. (3) Dry galvanizing, or keeping the iron in contact with metallic zinc dust, plus "blue dust," a by-product from the zinc smelter, in a drum at a certain temperature for a given length of time. The zinc alloys superficially with the iron, presenting a very tenacious coating, which resists corrosion well.

**HARDENING AND TEMPERING STEEL.**—After soft steel has been shaped into the form of instrument desired, it may be made *full hard,* by first heating to redness and then immediately chilling by plunging into cool water, oil, or mercury. If, however, the hardened steel be heated to redness again and allowed to cool slowly, it returns to its soft condition. Any desired variation between these two extremes may be obtained by heating the steel to redness and quickly chilling it, thus obtaining the full hard state. If this be polished and heated gradually and carefully, it will be found to take on a succession of shades and colors, owing to the formation of a film of oxide which grows thicker and of deeper shade and color as the heating progresses. The temperature at which given degrees of *temper* are produced has been carefully determined, and the experienced operator knows by the shade or color of the film of oxide the temper of the instrument operated upon, provided the piece is known to be steel and to have been full hard.

The following table shows the approximate temperatures corresponding to the various shades and colors:

| Temperature | Color | Temper |
|---|---|---|
| 220° to 238° C. | Very faint yellow to pale straw.. | Lancets, razors, surgical instruments, enamel chisels... |
| 243° ..... | Full yellow ..... | Excavators, very small cold chisels. |
| 254° ..... | Brown ..... | Pluggers, scissors, pen-knives. |
| 265° ..... | Brown with purple spots ..... | Axes, plane irons, saws, cold chisels. |
| 276° ..... | Purple ..... | Table knives, large shears. |
| 287° ..... | Bright blue..... | Swords, watch springs. |
| 292° ..... | Full blue..... | Fine saws, augers. |
| 315° ..... | Dark blue..... | Hand and pit saws. |

Since the amount of hardness which can be developed in steel is directly in proportion to the amount of carbon and rate of cooling the article from the heated condition, and as pieces of steel vary greatly in their content of carbon, the temperature at which it is necessary to heat them before chilling must be determined by actual experiment, in order to produce the greatest hardness. The piece should never be overheated. It is better to err upon the side of under- instead of over-heating, for under the latter condition the steel is *burned,* presents a blistered, scaly appearance, and is incapable of taking a fine temper. When small instruments, such as burs, excavators, etc., are to be hardened, it is best to protect the surface of the steel with some substance to prevent a loss of carbon by oxidation in the heating. "Common soap answers admirably for this purpose," says Dr. Kirk.

The means of applying the heat to articles when they require hardening will, of course, depend upon the size, shape, and use of the article. They may be heated in

the flame of a Bunsen burner, alcohol lamp, open fire, and sometimes it is best to enclose them in a sheet-iron case with carbon, and heat in a suitable furnace; but for a more uniform degree of heat red-hot lead is probably better than any other means.

In chilling, water is by no means essential, as the sole object is to extract the heat as rapidly as possible by good conduction; and the more suddenly the heat is extracted, the harder the steel will be; but if the hardness is not carried to an extreme, a certain amount of tenacity is also obtained with the hardness.

Water with a small amount of acid or salt is sometimes used, the former to aid in removing the oxide, and the latter to increase the conductivity. For extreme hardness mercury is used, which, on account of its superior conductivity, chills the piece immediately.

**TEMPERING.**—A rod of good steel in its hardest state is broken almost as easily as a rod of glass of the same dimensions. This brittleness can only be diminished by decreasing its hardness; and the management of this is called *tempering*. The surface of the steel is brightened and tried with a fine file to make sure of its full-hardness, and is then exposed to the heat, which, upon the appearance of the color desired and previously determined upon, is discontinued, and the article cooled by instantly plunging into cool water. The methods for applying the heat for tempering are as varied as those for hardening. The heat for this purpose should be slowly applied; indeed, it is said that the slower the heating, the tougher and stronger will be the steel. The article may be placed upon a hot iron plate, upon the surface of melted lead, or in a bath of a more fusible alloy (previously coating the instrument with

a solution of ochre in water, or liquid silex to prevent the adhesion of the molten metal), in hot sand, a gas stove, or in almost any place where sufficient temperature may be gradually obtained, without injury to the steel.

The following table of alloys of lead and tin may be conveniently used to secure a uniform temper:

| Composition | | Melting Points Degrees C. |
|---|---|---|
| Lead | Tin | |
| 7. | 4 | 210° |
| 7.5 | 4 | 221° |
| 8.5 | 4 | 232° |
| 10. | 4 | 243° |
| 14. | 4 | 254° |
| 19. | 4 | 265° |
| 30. | 4 | 276° |
| 48. | 4 | 287° |
| 50. | 4 | 293° |
| Boiling oil... | | 315° |

When instruments are only partially dipped and afterwards tempered by the heat from the back, they must be cooled in water, or other substance, instantly on the cutting part attaining the desired color; otherwise the body of the instrument will continue to supply heat, and the cutting part may become too soft. In the case of excavators, enamel chisels, and cutting instruments with slender, tapering shanks, terminating in a fine cutting edge, the edge must be protected from the heat while tempering the shank, the latter being drawn to a blue, a state much too soft for the former. The point or edge may be protected by placing against a large piece of cold iron or other substance, which, on account of its conduction, prevents the heating of the end of the instrument.

Rubber-dam clamps are best tempered a blue spring

by what is known as *blazing off*. This is accomplished by dipping them in oil, and then burning the oil off.

**COMPOUNDS WITH OXYGEN.**—Iron forms three compounds with oxygen:

*Monoxide,* Ferrous Oxide, FeO, is a very powerful base, but is almost unknown in the separate state on account of its tendency to absorb oxygen and pass into the sesquioxide.

**Sesquioxide,** or *Ferric Oxide,* $Fe_2O_3$, is a weak base and occurs native in most beautiful crystals as specular iron ore; also as red and brown hematite. It may be artificially prepared by precipitating a solution of ferric sulphate or chloride with excess of ammonia, washing, drying and igniting the yellowish-brown hydrate thus produced. It is of a red color, the tint varying with the temperature at which it has been exposed. It occurs commercially under the name of *colcothar jeweler's rouge,* and *Venetian red,* which is obtained by calcining the green sulphate of iron—

$$2(FeO.SO_3) = Fe_2O_3 + SO_2 + SO_3.$$

It is dissolved in acids with difficulty, forming a series of reddish salts.

**Triferro-tetroxide,** *Ferroso-ferric Oxide,* $Fe_3O_4$, is also called *black iron oxide, magnetic oxide,* and *loadstone.* It occurs native, and is one of the most valuable of the iron ores. It is the chief product of the oxidation of iron at a high temperature in the air and in aqueous vapor.

**ACTION OF ACIDS ON IRON.**—Iron dissolves in the acids, and the carbon which it always contains, so far as combined in the carbide of iron, passes off as carburetted hydrogen, and so far as uncombined will remain undissolved, as graphite.

In **dilute sulphuric acid** iron dissolves, forming ferrous sulphate, liberating hydrogen—

$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

In **hydrochloric acid** it dissolves, to form ferrous chloride, with liberation of hydrogen.

In **nitric,** cold and dilute, it is soluble, forming ferrous and ammonium nitrate—

$$4Fe + 10HNO_3 = 4Fe(NO_3)_2 + H_4NNO_3 + 3H_2O,$$

and in warm, dilute nitric to form ferric nitrate, liberating nitric oxide—

$$2Fe + 8HNO_3 = Fe_2(NO_3)_6 + 2NO + 4H_2O.$$

**ALLOYS.**—Iron combines with many of the metals. None of its alloys are of any great importance.

With **mercury,** iron can not be made to combine directly, yet Bloxam claims that it forms a chemical combination with this element, having the formula FeHg. The combination is effected by adding a little amalgam of sodium to the metallic mercury. The amalgam may also be prepared by "rubbing together very finely divided iron with mercuric chloride and water and a few drops of metallic mercury. Pure amalgam of iron forms lustrous white crystals, which, however, soon become coated with rust. By lying in the air the iron contained in the amalgam is in a short time converted into ferric oxide, which floats upon the metallic mercury."*

It alloys somewhat with the noble metals; also with tungsten, titanium, chromium, and manganesium.

*Brannt, Metallic Alloys, p. 363.

An alloy of cast iron 79, tin 19.50, and lead 1.50, may be used as a casting metal, giving fine impressions, filling the molds, and being malleable to a certain extent.

**Arnold's Iron Alloy.**—Crude cast iron, 100; soda, 1; copper, 1; tin, 5; antimony, 5; and zinc, 5. A compact and malleable alloy, capable of taking a fine polish, and resisting the corrosive action of sea water. It is used for ship propellors.

**Marle's Nonoxidizable Alloy.**—Iron, 10 parts; nickel, 35; brass, 25; tin, 20, and zinc, 10.

**TESTS FOR IRON IN SOLUTION.—Ferrous salts.**—The solutions are *green,* and sulphuretted hydrogen produces no precipitate in an acid solution, but may give a slight one in a neutral solution.

**Ammonium hydrosulphide** gives a black precipitate of ferrous sulphide, insoluble in excess of the precipitant.

**Potassium ferricyanide** is the characteristic test; it throws down a deep blue precipitate (Turnbull's blue).

$$K_6Fe_2(Cn)_{12} + 3FeCl_2 = 6KCl + Fe_3Fe_2(Cn)_{12}.$$

**Ammonia** throws down hydrated ferrous oxide (the antidote for arsenic*). This is, at the moment of formation, white, but passes rapidly through the shades of light green, dark green, and ultimately brown, the latter being an indication of its conversion into ferric oxide.

**Ferric Oxide.—Potassium ferrocyanide** is a characteristic test, producing a precipitate of Prussian blue.

$$3[K_4Fe(Cn)_6] + 4FeCl_3 = 12KCl + Fe_43[Fe(Cn)_6]$$

*It should be the invariable rule of every dentist to keep on hand in his office the materials for preparing this antidote, for an emergency, as it should be freshly prepared at the time of need. A very efficient antidote may be prepared by precipitating the tincture of the chloride of iron with bicarbonate of sodium.

# CHAPTER XIV

## ALUMINUM

| | |
|---|---|
| Aluminum. | Symbol, Al. |
| Valence $(Al_2)^{VI}$ | Specific gravity, 2.583 at 4°. |
| Atomic weight, 27.1. | Malleability, 4th rank. |
| Melting point, 657° C. | Tenacity, good. |
| Ductility, 7th rank. | Chief ore, cryolite. |
| Conductivity (heat), 34.35. | Conductivity (electricity), 63.0. |
| (Silver being 100.) | |
| Specific heat, 0.2220. | Crystals, octahedral. |
| Color, bluish-white. | |

**OCCURRENCE.**—With the exception of silicon and oxygen, aluminum is the most abundant element in the earth's crust. It is never found in the free or metallic state, but occurs combined with silicon and oxygen, as marl, clay, slate, pumice stone, feldspar, mica, and nearly all rocks, with the exception of limestone and sandstone. As the crystallized oxide—*alumina*—it occurs as corundum, emery, ruby, sapphire, emerald, topaz, and amethyst, which are used as gems. The metal is further found in combination with nearly two hundred different minerals. Dana gives the formula for the principal ores as:

| | |
|---|---|
| Cryolite | $Na_3AlF_6$ |
| Corundum | $Al_2O_3$ |
| Gibbsite | $Al(OH)_3$ |
| Bauxite | $Al_2O(OH)_4$ |
| Kaolin | $H_4Al_2SiO_9$ |
| Feldspars | $KAlSi_3O_8$ |
| | $NaAlSi_3O_8$ |
| | $CaAl_2Si_2O_8$ |

**REDUCTION.**—It was first isolated in 1827 by Wöhler, who obtained it as a gray powder by decomposing aluminum chloride with potassium. It remained a laboratory product until St. Claire Deville, about 1858, succeeded in improving the mode of production, so as to render the operations capable of management on a manufacturing scale. The process consists in heating to a red heat the double chloride of aluminum and sodium with metallic sodium. A vigorous action takes place, chloride of sodium being formed and the metallic aluminum separated—

$$AlCl_3.NaCl + 3Na = Al + 4NaCl.$$

The chemical processes are now practically replaced by electrolytic methods of reduction.

Chas. M. Hall,* an Ohio college student, conceiving it possible to extract aluminum from its ores by electrolysis, set to work to accomplish the task. Recognizing the impossibility of attaining practical results from an aqueous solution, he sought other solvents, and finally discovered that a melted bath of the double fluorides of aluminum and metals more electropositive than aluminum, such as sodium or calcium, was a perfect solvent for alumina, the oxide of aluminum, taking it up as hot water dissolves sugar, and dissolving as much as 25 per cent of its weight. Having found an anhydrous solvent for alumina, the discoverer next sought to ascertain whether the solution would yield up the aluminum promptly to electrolysis. Great suc-

*On January 20, 1911, Chas. M. Hall received the Perkins medal, granted to a chemist residing in the United States for valuable work in applied chemistry. His company, the Aluminum Company of America, has five large plants, consuming 140,000 horse power of electricity, more than any other single company in the world. The annual output in 1910 was 40,000,000 tons and the price has dropped from $90.00 a pound in 1855 to 22 cents a pound in 1910.

cess attended his experiments in this particular and by superior intelligence and great patience Hall worked out the practical application of his discovery. At present his company has two plants at Niagara which combined are capable of yielding about 10,000 pounds in twenty-four hours.

**PROPERTIES.**—Aluminum is a bluish-white metal somewhat resembling silver in appearance. It ranks fourth in malleability, seventh in tenacity, and ranks next to gold in the conduction of heat and electricity. It is harder than tin, but softer than copper. By hammering in the cold it may be made as hard as soft iron, but is softened again by fusion. It is remarkably sonorous, and has been used for making bells. It is one of the lightest of metals, being approximately only 2½ times heavier than water, and ¼ the specific gravity of silver. It fuses at 657° C., and when cold oxidizes superficially on exposure to the air. It has no action on water at ordinary temperatures, nor is it acted upon by the compounds of sulphur, thus preserving its luster where silver would tarnish and blacken. It is without odor or taste.

Aluminum may be melted in an ordinary clay crucible, using zinc chloride as a flux. Aluminum oxide forms as a thick pasty mass, is impossible to skim, and when it enters the castings weakens them. Dry $ZnCl_2$ is used in small pieces, stirring each time, until surface is mirrorlike, when enough has been used. The black dross should be skimmed before casting.

**IN THE ARTS** aluminum is used in the manufacture of weights of small denomination, such as the milligram. Its low specific gravity renders it particularly well adapted to such use. It is further used, on account of

its lightness and resistance to atmospheric action, for the manufacture of delicate physical, mathematical, and optical apparatus, as well as ornamental articles, such as medallions and badges of a souvenir character; also for parts of bicycles, tablewear, and cooking utensils.* The apex of the Washington Monument is of highly polished aluminum.

**IN DENTISTRY** this metal is employed as a base for artificial dentures. Its many valuable properties, chiefly conductivity, lightness, malleability, cheapness, and unalterableness in dry or moist air, render it applicable for such a purpose. The base is swaged between a zinc die and a lead counterdie, but will not stand the rough swaging usually given to gold or platinum. Caution must be used to prevent contamination with the lead or zinc. It being difficult to determine during the progress of the conformation whether or not any contamination has occurred, the pattern is best swaged between sheets of thin tissue paper, removing the paper as it becomes broken. The metal should be occasionally annealed by coating with pure sweet-oil or tallow and passing through the flame until the oil or fat is carbonized, when at the moment the last trace of black (carbon) disappears from the metal, it may be dropped into water. Before applying the oil and annealing, however, the metal should be thoroughly brushed with pumice stone, to remove any contaminating lead or zinc which might otherwise become alloyed with the base, causing small holes or pits to appear on its surface, or perhaps the occurrence of galvanic action. A simpler and cleaner method of annealing is

*Experiments to determine the effect of food upon cooking utensils showed that aluminum was strongly attacked by $NaHCO_3$, $MgSo_4$ and mineral waters only.

to heat the metal in a Bunsen flame until it is hot enough to show a streak of carbon when a dry pine stick is rubbed across it. Then cool it slowly.

Vulcanite is attached to such a base by spurs made with a sharp-pointed graver, countersunk holes, or loops made with a punch along the alveolar ridge. After waxing up the denture the base may be varnished to protect it from the plaster during vulcanization, after which the varnish is removed with alcohol, and the plate polished with pumice stone and whiting, but it can not be well burnished.

The process of making cast aluminum dentures was first introduced by Dr. J. B. Bean of Baltimore, who cast the metal through tall conduits lined with clay and attached to the gates of his flask, the entire apparatus being first heated to an elevated temperature. The pressure of the column of metal thus produced overcame the sluggish flow due to an inherent lack of fluidity and lightness of the metal, and forced it into the finer parts and irregularities of the mold.

The cast bases were abandoned for a long time because of corrosion and decomposition in the mouth, but with the advent of improved methods of casting the use of cast aluminum for dentures has been revived with success.

**THE COMPOUND WITH OXYGEN.—Aluminum oxide,** *Alumina,* the *Sesquioxide of Aluminum,* $Al_2O_3$, is found crystallized in hexagonal prisms in nature, as ruby, sapphire, corundum,* etc., colored by admixtures. It may be prepared by treating a solution of alum with

*Chemical formulæ of some of the oxides of aluminum:
Corundum .....(Ruby and sapphire the same) $Al_2O_3$.
Garnet .....$(CaMgFeMn)_3Al_2Si_3O_{12}$.
Cyanite .....$Al_2SiO_5$.

an excess of ammonia, by which an extremely bulky, white, gelatinous precipitate of aluminum hydrate is formed. This is washed, dried, and ignited to whiteness. Thus obtained, alumina constitutes a white, tasteless, feebly basic coherent mass, very little acted upon by acids, and fusible in the oxyhydrogen flame. *Emery* is impure corundum, containing iron and aluminum oxides.

**Feldspar** is regarded as the double silicate of potassium and aluminum, a natural glass and as having the formula $Al_2O_3.K_2O.6SiO_2$. It is much used in the preparation of bodies, frits and enamels for the manufacture of porcelain.

**Kaolin,** china clay, is known as a hydrated silicate of aluminum, $(2Al_2O_3.3SiO_2) + 3H_2O$, and is the purest form of clay. It results from the decomposition of feldspar by the weathering out of the potassium hydroxide (KOH). It is practically infusible and forms the refractory substance of fine porcelain, being much used in the preparation of bodies for the manufacture of dental porcelain.

**Porcelain.**—The typical porcelain may be regarded as a fused mixture of the fusible feldspar, binding together the particles of the infusible kaolin in a homogeneous mass.

**ACTION OF ACIDS AND ALKALIES ON ALUMINUM.**—Sulphuric acid, concentrated and boiling, dissolves aluminum, but it is not soluble in the dilute acid.

**Nitric acid** does not affect aluminum.

**Hydrochloric acid,** hot or cold, readily dissolves it, forming aluminum chloride, and evolving hydrogen—

$$2Al + 6HCl = Al_2Cl_6 + H_6.$$

**In Potassium or sodium hydrate** it is soluble, forming aluminates and liberating hydrogen—

$$Al + 3KHO = K_3AlO_3 + H_3.$$

**ALLOYS.**—Aluminum alloys with nearly all metals, except lead; indeed, the wonderful alloys it is capable of producing gives it, perhaps, its greatest value.

Aluminum may be melted in a graphite crucible without flux, but great care must be taken not to heat it too hot. On account of its high specific and latent heat, aluminum requires a long time to melt; but, unlike some other metals, it soon becomes fluid after the melting point is reached.

With **mercury** alone aluminum is said to form an unstable amalgam. The experiments made by Dr. Black showed aluminum in the proportion of 1 to 5 per cent in silver-tin amalgam alloys to so increase the expansion in amalgams made of them as to exclude this metal as a component in dental-amalgam alloys. Mercury in contact with aluminum tends to expose the latter to the action of the air, probably by destroying the superficial oxide of aluminum which normally prevents further oxidation. This action will continue until the surface of the aluminum is deeply pitted or eroded, and is marked by repeated growths of aluminum oxide at the point of contact.

**Gold** and aluminum unite, forming a hard and brittle alloy. One per cent of aluminum in gold destroys the ductility of the noble metal and gives it a greenish cast; 5 per cent of aluminum with gold yields an alloy brittle as glass, and 10 per cent of aluminum

produces a grayish white, crystalline and brittle alloy.

**Nürnberg gold,** an alloy, for cheap goldware, very much resembling gold, and unchanged in air, is composed of aluminum 7.5, gold 2.5, and copper 90 parts.

**Silver** and aluminum readily unite, forming alloys of beautiful whiteness and unchangeable on exposure to air. Their hardness is considerably greater than aluminum, but they are more easily worked. An alloy of 100 parts of aluminum and 5 parts of silver differs but little from pure aluminum, save that it is considerably harder and takes a beautiful polish. An alloy of aluminum 169 parts and silver 5 parts possesses considerable elasticity, and has been recommended for springs, dessert and fruit knives. Equal parts of the two metals produce an alloy equal to that of bronze in hardness.

**Copper** and aluminum form some exceedingly important alloys, differing according to the quantity of aluminum they contain. Those of a small content of copper can not be used industrially. With 60 to 70 per cent aluminum they are very brittle, glass-hard, and beautifully crystalline. With 50 per cent the alloy is quite soft; but under 30 per cent of aluminum the hardness returns. The usual alloys are 1, 2, 5, and 10 per cent of aluminum. These are known as *aluminum bronze.* The 10 per cent bronze has a bright golden color, and retains its polish when exposed to air; it may be easily engraved, exhibits a great elasticity, and can be easily soldered with 18-carat gold solder. When first made, it is brittle, acquiring its best qualities after three or four meltings, after which it may be melted several times without sensible change. It casts well in sand molds, but shrinks greatly. It has a specific grav-

ity of 7.68, about equal to soft iron. Its strength when hammered will equal that of the best steel. Annealing makes it soft and malleable. It does not clog a file, and may be drawn into a wire. It melts at about 927° C.

Aluminum bronze as a base for artificial dentures: In the proportion of aluminum 10 and copper 90 it oxidizes but superficially in the mouth, and is as strong and resistant to attrition as 18-carat gold, it may be swaged as easily as 20-carat gold, but it must be annealed frequently, and it is necessary to carry the heat almost to whiteness, for if the bronze be merely heated until it assumes a dark-red color, it remains as hard as before.

**Zinc** is the cheapest known hardener of aluminum. It increases rigidity and strength up to 15 per cent zinc. Zinc chloride is the best flux for molten aluminum, the metal subsequently showing a trace of zinc. An analysis of the alloys used in the construction of Zeppelins shows: aluminum, 88 to 90 parts; zinc, 7 to 9 parts; copper, 7 to 9 parts, and a small amount of tin, iron, silicon, and manganese.

Aluminum and magnesium produce an alloy with a specific gravity of about 1.75. It is hard, can be turned and drilled, is much tougher than brass and has a tensile strength equal to it, yet is extremely malleable. It can be drawn into wire and rolled and beaten like silver.

**Solders.**—There is no solder which operates with aluminum in the same way that ordinary solders operate with copper, tin, etc. The reasons are because aluminum does not alloy readily with other metals at low temperatures, and its surface becomes coated with an

invisible oxide, very refractory, and insoluble in almost everything except hydrofluoric acid. This oxide must be removed by mechanical abrasion while the solder is in position in a fluid state.

A steel or brass scratch brush may be used while the solder is in a molten state. Zinc appears to alloy more readily with aluminum than any other metal. Tin, zinc and a very small proportion of aluminum is a very effective solder. It requires a blast flame and does not run freely. It will not flow by capillary attraction, and enough solder must be placed on the joint to sweat it together before bringing edges in contact.

Wm. Frismuth of Philadelphia recommends the following solders for aluminum, with vaseline as the flux:

SOFT SOLDER

| | | | | |
|---|---|---|---|---|
| Pure Block Tin..... | from | 90 | to | 99 parts |
| Bismuth ..... | " | 10 | " | 1 " |

HARD SOLDER

| | | | | |
|---|---|---|---|---|
| Pure Block Tin..... | from | 98 | to | 90 parts |
| Bismuth ..... | " | 1 | " | 5 " |
| Aluminum ..... | " | 1 | " | 5 " |

Schlosser recommends the following for dental laboratory use:

PLATINUM-ALUMINUM SOLDER

| | |
|---|---|
| Gold ..... | 30 parts |
| Platinum ..... | 1 " |
| Silver ..... | 20 " |
| Aluminum .....100 | " |

GOLD-ALUMINUM SOLDER

| | |
|---|---|
| Gold ..... | 50 parts |
| Silver ..... | 10 " |
| Copper ..... | 10 " |
| Aluminum ..... | 20 " |

O. M. Thowless has patented the following solder for aluminum and method for applying it.

| | |
|---|---|
| Tin | 55 parts |
| Zinc | 23 " |
| Silver | 5 " |
| Aluminum | 2 " |

First melt the silver and aluminum together, then add the tin and zinc in the order named. The surfaces to be soldered are immersed in dilute caustic alkali or a cyanide solution, and then washed and dried. They are next heated over a spirit lamp, coated with the solder, and clamped together, small pieces of solder being placed at the points of union; the whole is then heated to the melting point. No flux is used. The following are useful as solders:

| | I | II | III |
|---|---|---|---|
| Zinc | 80 parts | 85 parts | 92 parts |
| Aluminum | 20 " | 15 " | 8 " |

The flux used in soldering is composed of 3 parts balsam of copaiba, 1 part Venetian turpentine, and a few drops of lemon juice. The soldering iron is dipped into the mixture.

Another solder for aluminum, recommended by the *Scientific American*, is composed of the following:

| | |
|---|---|
| Cadmium | 50 parts |
| Zinc | 20 " |
| Tin | 30 " |

The zinc is first melted in a suitable vessel; then the cadmium is added, and then the tin, in small pieces.

The proportions of the various ingredients may be varied, in accordance with the use to which the article is put. For instance, when a strong and tenacious soldering is required, a larger proportion of cadmium can

be used; where great adhesion is desired, a large proportion of zinc should be used, and where a nice and durable polish is desired, a greater per cent of tin should be used.

An alloy of zinc, copper, and aluminum has been introduced as a dental base. It is said to be unaffected by the oral fluids.

**Tin** and aluminum form alloys little affected by acids. With 100 parts aluminum and 10 parts tin an alloy is produced much whiter than aluminum and but little heavier. It can be welded and soldered like brass.

**Iron** and aluminum unite readily. Ostberg, a Swedish inventor, discovered that an exceedingly small content of aluminum (0.005 of 1 per cent) in wrought iron served to lower its fusing point about 500° F., so that castings may be made from it as readily as from the highly carburized cast iron. Iron may be coated with aluminum much as it is with tin.

**Zinc** and aluminum unite to form alloys very useful for soldering the latter. They are prepared by first melting the aluminum and adding the zinc gradually, after which some fat is introduced to prevent oxidation, and the alloy is stirred rapidly with an iron rod. Aluminum may be frosted by immersion in a solution of potassa.

**TESTS FOR ALUMINUM IN SOLUTION.—Sulphuretted hydrogen** does not produce a precipitate when added to a solution of a salt of aluminum.

**Ammonium hydrosulphide** produces a white precipitate of aluminum hydrate and evolves sulphuretted hydrogen.

**Ammonium hydrate** throws down a bulky, gelatinous aluminum hydrate, slightly soluble in the precipitant.

# CHAPTER XV

## MERCURY

| | |
|---|---|
| Hydrargyrum. | Symbol, Hg. |
| Valence, II ($Hg_s$) II. | Specific gravity, 13.595. |
| Atomic weight, 200.6. | Malleable at —38.85 C. |
| Melting point, —38.85. | |
| Boiling point, 357.3° C. | |
| Conductivity (heat), 1.48. | Conductivity (electricity), 1.6. |
| Specific heat, 0.0337 at 0° C. | Chief ore, cinnabar. |
| Color, silver-white. | Crystals, octahedral at —39° C. |

**OCCURRENCE.**—Mercury occurs in nature chiefly as the red sulphide, HgS, *cinnabar,* which, as a rule, is accompanied by more or less of the reguline metal. The most important mercury mines of Europe are those of *Almaden,* Spain, and of Idria, in Illyria; it is also found in China, Mexico, Corsica, Peru, and California. The European mines, until lately, furnished the bulk of the mercury of commerce, but they have been eclipsed by the rich deposits of *New Almaden,* near San José, California. The mines of the latter have been the most productive in the world, yielding more than 3,000,000 pounds annually, and large quantities are still taken from them. The California cinnabar is richer in mercury, because purer, than the Spanish, the former yielding about 70, the latter about 38 per cent of mercury.

Mercury is also found *free;* forming an *Amalgam* with silver and in the form of protochloride (native *calomel*).

**REDUCTION.**—The metal is obtained almost exclusively from the sulphide or native cinnabar, and is extracted by two principal methods. By the first

method the mineral is picked, crushed, and mixed with lime. The mixture is then introduced into cast-iron retorts, which are placed in rows, one above the other, in an oblong furnace and connected with earthenware receivers, one-third full of water. Heat is applied, the lime combines with the sulphur, forming the sulphide and sulphate of calcium—

$$4HgS + 4CaO = 3CaS + CaSO_4 + Hg_4,$$

while the mercury distills over, and is condensed in the receivers. In the second method the decomposition of the cinnabar is effected by the direct exposure of the ore to the oxidizing flame of the furnace, and the mercury vapor is recovered in more or less imperfect condensers.

**PURE MERCURY.**—The commercial article, as a rule, is quite pure chemically, and only needs to be forced through chamois skin to be fit for ordinary purposes; but it frequently contains foreign metals, such as lead, tin, zinc, and bismuth. It is seldom intentionally adulterated. When impure, the metal has a dull appearance, leaves a trace on white paper, is deficient in due fluidity and mobility, which is shown by its inability to form perfect globules, is not totally dissipated by heat, and, when shaken in a glass bottle, coats the sides with a pellicle, or, if very impure, deposits a black powder. If agitated with strong sulphuric acid, the adulterating metals become oxidized and are dissolved, thus the metal may be to a limited extent purified.

**Detection of Lead.**—Lead may be detected by shaking the suspected metal with equal parts of acetic acid and water, and then testing the acid with sulphate of

sodium, or iodide of potassium. The former will produce a white, the latter a yellow, precipitate, if lead be present.

**Detection of Bismuth.**—Bismuth is shown by dropping a nitric acid solution of the mercury, prepared without heat, into a quantity of distilled water, when, if bismuth be present, the subnitrate of bismuth will be precipitated.

**Detection of Tin.**—Complete solubility of the metal in nitric acid shows the absence of tin.

Lead is the chief impurity, and may be removed by exposing thin layer of the metal to the action of nitric acid diluted with twice the quantity of water, which should well cover the surface and remain a day or two, with frequent stirring. The lead is much more easily oxidized and dissolved than the mercury, though some of the latter also passes into solution. The mercury is afterwards well washed with water, and dried first with blotting paper, then by gentle heat. In the same manner most of the other metallic impurities are removed. Mercury for dental use should, however, be purified by redistillation.

Chemically pure mercury may be obtained by decomposing pure mercuric oxide by heat, and washing the condensed metal with dilute nitric acid.

**PROPERTIES.**—Mercury or *quicksilver,* as it is often called, is of a silver-white color, liquid at ordinary temperature (above —38.85), odorless and tasteless. It is volatile at ordinary temperatures, but more rapidly volatilizes as the temperature increases. At 357.3° C. it boils, being finally volatilized without residue. When globules are dropped upon white paper,

they should roll about freely, without tailing, retaining their globular form. It should be perfectly dry, and present a bright surface. When perfectly pure it undergoes no alteration by the action of the air or of water, but in the ordinary state it will exhibit a slight tarnish. It solidifies at —38.85° with considerable contraction into a compact mass of regular octahedra, which can be cut with a knife, or flattened under the hammer.

**USES.**—It is constantly required in the chemical laboratory, and is greatly used in the construction of thermometers, barometers, and manometers, for the determination of the capacity of vessels, and for many other purposes.

**In medicine,** in the uncombined state, it is inert, but in combination acts as a peculiar and universal stimulant. When exhibited in the finely divided state, it forms several preparations, producing peculiar effects; this fact, however, does not prove that the uncombined metal is active, but that in minute division it is favorable to chemical action and combination. Rubbed up with chalk, mercury forms *hydrargyrum cum creta;* with the confection of roses and licorice, *massa hydrargyri;* with lard and suet, *unguentum hydrargyri.*

**Mercurial poisoning,** ptyalism, salivation, is first observable by a coppery taste, a slight soreness of the gums, and an unpleasant sensation in the alveoli of the teeth, when the jaws are firmly closed.

In **dentistry** mercury is used to form alloys known as amalgams. (See chapter on Amalgams.)

**COMPOUNDS WITH OXYGEN.—Monoxide,** or *Mercuric Oxide,* HgO, perhaps more commonly known as *red oxide of mercury,* or *red precipitate.* The compound

may be prepared by several methods, the most prominent of which are: *First,* by exposing mercury in a glass flask with a long, narrow neck, for several weeks, at a temperature of about 315° C. The product of such exposure and heat is highly crystalline and of a *dark red* color. *Second,* as it is generally prepared, by cautiously and thoroughly heating any of the mercuric or mercurous nitrates to complete decomposition, which latter fact is recognized by the absence of the characteristic red fumes and odor of nitric oxide. By this means the acid is decomposed and expelled, oxidizing the metal to the maximum if it happens to be in the state of mercurous salt. The product thus obtained is also crystalline and very dense, but of a much paler color than the preceding. While hot, it is nearly black. *Third,* by adding caustic potash in excess to a solution of mercuric chloride, by which a bright yellow precipitate of mercuric oxide is thrown down. This precipitate is destitute of crystalline character, and much more minutely divided than the two preceding.

The monoxide is only slightly soluble in water, communicating to the latter an alkaline reaction and metallic taste; it is highly poisonous. When strongly heated, it is decomposed into mercury and oxygen gas.

**Mercurous Oxide,** $Hg_2O$; *Suboxide* or *Gray Oxide of Mercury,* may be prepared by adding caustic potash to mercurous nitrate. It is a dark gray, nearly black, heavy powder, insoluble in water, slowly decomposed by the action of light into metallic mercury and the red oxide.

**ACTION OF ACIDS ON MERCURY.—Hydrochloric acid** does not attack mercury.

**Sulphuric acid,** boiling, converts it into mercurous sulphate, liberating sulphur dioxide.

**Nitric acid,** is the most effective solvent for mercury. It dissolves readily in the dilute acid if heated, or in the cold, if nitrous acid is present; with the strong acid, heat is soon generated, and with considerable quantities of the material the action acquires an explosive violence. At ordinary temperatures, dilute nitric acid, when applied in slight excess, produces chiefly normal mercurous nitrate, but when the mercury is in excess, more or less of basic mercurous nitrate is formed; hot dilute nitric acid, in excess, forms chiefly mercuric nitrate; when the mercury is in excess, both basic mercurous and basic mercuric nitrates are formed. In all cases, chiefly nitric oxide gas is evolved.

**ALLOYS.**—Mercury unites readily with most metals except *iron* and *platinum*. With the former it has been found to unite only indirectly; for example, by rubbing very finely divided iron with mercuric chloride, water, and a few drops of metallic mercury. The latter metal can only be combined in the *spongy* state. Yet both of these metallic elements combine chemically with mercury to form definite compounds, according to Bloxam and other authorities, and present the composition, FeHg and $PtHg_2$, respectively.

Of **gold** and mercury, Dr. H. H. Burchard,* in an exceptionally able paper, quotes:

"A gold amalgam 1 to 1000 has all the fluid mercury expressed through chamois; the residue treated with dilute nitric acid at a moderate heat. A solid amalgam

*Dental Cosmos, xxxvii, p. 989.

is left, $Au_8Hg$, which crystallizes in four-sided prisms, and does not melt even when heated until the mercury volatilizes."* And further, "A mixture of gold and mercury was heated to a temperature a little above the boiling-point of mercury, and the heat maintained until the weight became constant, and there resulted an amalgam containing 10.3 per cent of mercury, giving a formula of $Au_9Hg$." (Hiorns.)

Then adds: "Guettier points out that a saturated solution of gold in mercury is $Au_2Hg$, a mass of waxy consistence. Evidently, when the gold exceeds this ratio, there is not a perfect chemical compound, as, for instance, in the $Au_8Hg$ amalgam."

**Silver** and mercury combine very readily, and undoubtedly from a definite chemical compound. Joulé gives its formula as $Ag_2Hg_,$, Bloxam as $Ag_2Hg_3$. It also forms two native amalgams having the formulæ of AgHg and $Ag_2Hg_6$.

With **copper, zinc, tin,** and **lead** it also forms definite chemical compounds, and their formulæ may be expressed respectively as: CuHg, $Zn_2Hg$, $Sn_2Hg$, and $Pb_2Hg$. The conclusion, then, is obvious that our dental amalgams are probably mostly—fundamentally, at least—chemical compounds, but usually with mercury, and, perhaps, some other constituent in excess.

**VERMILION.**—Mercuric sulphide, HgS, occurs native as cinnabar, a dull-red mineral, the most important ore of mercury. It may be prepared by several different methods, much depending upon the purity of the materials employed. When mercury and sulphur are heated together, the union is accompanied with much

*T. H. Henry, Philos. Mag., ix, p. 468.

energy, and if the product be sublimed, becomes the red or mercuric sulphide. The sulphur is best first melted and the mercury gradually added by straining through linen cloth, whereby it falls in a minutely divided state, while the mixture is constantly stirred. When the temperature arrives at a certain point, the combination takes place suddenly with a slight explosion, attended with the ignition of the sulphur, which must be extinguished by covering the vessel. The product of the combination is a black mass, generally containing an excess of sulphur, which, before the sublimation is performed, should be got rid of by gentle heat on a sand-bath. Sublimation is best carried on in a closely stoppered glass matrass, which should be placed in a crucible containing sand, and, thus arranged, exposed to a red heat. The resulting vermilion is reduced to a fine powder by levigation, the beauty of the tint depending much upon the extent to which the division is carried.

It is prepared in a wet way by intimately mixing 100 parts of mercury with 38 parts flowers of sulphur, and the black sulphide of mercury thus obtained digested with constant agitation, in a solution of 25 parts of caustic potash in 150 parts of water at 45° C. (the water lost by evaporation being constantly replaced), until the preparation has come up to its maximum of fire and brilliancy, which takes a good many hours. Purely sublimed vermilion has a comparatively dull color, and must be manipulated with an alkaline (potassium) sulphide solution to give it the necessary fire. The action of the alkaline sulphide consists probably in this, that it dissolves successive

installments of the amorphous preparation and redeposits them in the crystalline form.

**Properties.**—It is a fine, bright scarlet powder, permanent in air, odorless and tasteless, insoluble in water, alcohol, dilute nitric, concentrated hydrochloric, or sulphuric acids. Nor is it acted upon by boiling potassium hydroxide, sulphide of ammonium, cyanide of potassium or sulphite of soda. It is slightly acted upon by concentrated hot nitric acid, and completely soluble in a solution of potassium sulphide in the presence of free alkali or a solution of sodium sulphide. Nitrohydrochloric acid decomposes it into mercuric chloride, which is readily soluble. It may be completely sublimed, as has been seen, without decomposition, but if exposed to a temperature of 315.5° C. it is decomposed into metallic mercury and sulphur dioxide. It is frequently adulterated with red lead, dragon's blood, chalk, ferric oxide, realgar ($As_2S_2$), and brick-dust. If lead be present, it will yield a yellow precipitate when digested with acetic acid and potassium iodide added. Dragon's blood may be detected by alcohol, which will take up the coloring matter of that substance if present. Chalk is detected by an effervescence on the addition of an acid. Most other impurities may be detected by subliming a small portion of the compound. The nonvolatile substances used for adulteration will remain behind.

**Uses.**—When pure it is much used as a pigment, on account of its brilliancy and color. Its unalterableness and resistance to chemical action render it particularly valuable in giving the red color to vulcanizable rubber used in the construction of artificial den-

tures of red and pink vulcanite in the composition of which it forms, in some cases, about one-third of the entire weight of the compound. Notwithstanding the poisonous character of mercurial compounds in general, and the frequency of troubles of an inflammatory nature of the mucous membrane in mouths fitted with rubber dentures, it is obviously very improbable, when we consider the properties of pure vermilion, that such conditions can be in any degree attributable to the presence of this substance *per se*. It is quite possible that impure vermilion may contain from the start free mercury; be contaminated with arsenic bisulphide, or poisonous adulterations. Again, the practice of dissolving tin-foil off of the surface of plates with nitro-hydrochloric acid just after vulcanization may possibly decompose some little vermilion, forming soluble bichloride. It is highly improbable that any of these conditions can be found, yet it is possible. It is said that free mercury has been observed with the microscope in finished vulcanite. The occurrence of oral inflammatory conditions, under *black rubber* dentures, precisely similar to those under red rubber, practically relieves vermilion of the responsibility. Such inflammatory troubles are directly attributable to its *rough* and *porous* surface, *lack of cleanliness* on the part of the wearer, and the fact that rubber is a *nonconductor* of heat.

**TESTS FOR MERCURY IN SOLUTION.—Sulphuretted hydrogen,** gradually added to mercuric solutions, forms at first a white precipitate; by further additions of the reagent, the precipitate becomes yellow-orange, then brown, and finally black. Such progressive varia-

tion of color is characteristic of mercury. With mercurous compounds, sulphuretted hydrogen, and soluble sulphides precipitate mercurous sulphide, $Hg_2S$, black, without change of color.

Soluble **Iodides** precipitate mercuric iodide, $HgI_2$, from mercuric compounds, first reddish-yellow, then red. From mercurous solutions they precipitate mercurous iodide, $Hg_2I_2$, greenish-yellow in color.

**Caustic soda** or **potassa** precipitates yellow mercuric oxide from mercuric salts, and black mercurous oxide from mercurous salts.

**Ammonium hydrate** throws down a "white precipitate" of mercuric chloramide ($H_2NHgCl$) from mercuric salts, but black precipitates are thrown down from mercurous salts.

# CHAPTER XVI

## SILVER

| | |
|---|---|
| Argentum. | Symbol, Ag. |
| Valence I. | Specific gravity, 10.53. |
| Atomic weight, 107.88. | Malleability, 2d rank. |
| Melting point, 961.5. | Tenacity, 4th rank. |
| Ductility, 2d rank. | Conductivity (electricity), 100 |
| Conductivity (heat), 100. | Chief ore, silver glance. |
| Specific heat, 0.0559. | Crystals, isometric. |
| Color, white. | |

**OCCURRENCE.**—Silver is widely diffused throughout the earth's crust. It is found chiefly in the United States, Mexico, Peru, and Chile; Austria-Hungary, Norway, and Australia also furnish considerable amounts.

Of the varieties of silver ores the following chiefly are metallurgically important. (1) *Reguline silver,* (2) *horn silver,* (3) *silver glance,* (4) *silver-copper glance,* (5) *pyrargyrite,* (6) *stephanite,* and (7) *polybasite.* Silver is also frequently met with in base metallic ores, as in lead ores and many kinds of pyrites.

**Reguline Silver,** native silver. Owing to the weak affinity of silver for other substances it is frequently found free in a metallic state, occurring in flat masses, and at times in arborescent form, composed of numerous isometric crystals strung together, or in twisted filaments. In the Lake Superior district it occurs with native copper, showing in specks upon the surface of the latter metal. With mercury it is found as a native crystalline amalgam. Native silver is usually

free from any considerable admixture of other metals, but it always contains gold.

**Horn silver,** native chloride, AgCl. The ore is named from its resemblance to horn in texture and appearance. It is of a pearl-gray color when freshly cut, and on exposure to sunlight turns brown. It contains about 75.3 per cent silver. The corresponding bromide and iodide also occur native.

**Silver glance,** native sulphide, $Ag_2S$, is the most important ore of silver. It is a soft, gray, and somewhat malleable mineral, may be cut with a knife, is quite fusible, and when pure contains 87.1 per cent silver. It is frequently found associated with copper, as *silver-copper glance* $(AgCu)_2S$; with antimony, as *pyrargyrite,* $Ag_3SbS_3$, and as *stephanite,* $Ag_5SbS_4$, with copper, antimony and arsenic, as *polybasite,* $9(Ag_2,Cu_2)S + (Sb_2, As_2)S_3$; with lead, as *argentiferous galena,* and with iron.

**REDUCTION.**—The method by which silver is extracted from its ores depends chiefly on the nature of the admixtures, the state of the combination of the silver being as a rule irrelevant in the choice of process, because some of the noble metal is always present as a sulphide, and the mode of treatment for it includes all other forms.*

**Amalgamation.**—If the ore is comparatively free from base metals, amalgamation is resorted to. Most ores contain too great a proportion of earthy matter, etc., to admit of any other method economically, even in localities where fuel is plentiful. Several methods of amalgamation are employed, varying with different localities and circumstances, but the principles involved

*See also Cyanidation, chapter on Gold.

are similar, and a general description will suffice for all.

The ore is ground and roasted at a dull-red heat with common salt, which converts the sulphide of silver into chloride—

$$Ag_2S + 2NaCl + 2O_2 \text{ (from the air)} = 2AgCl + Na_2SO_4.$$

Fig. 46.—A primitive Philippine Arastra; the same type was used by the Spaniards and Mexicans and the process of reduction was very similar to the chloridizing and amalgamation process.

The mass, along with certain proportions of water, scrap-iron, and mercury, is placed in barrels, which are made to rotate about their axis, so that the several ingredients are forced into constantly varying contact with each other. The salt solution takes up a small proportion of the chloride, which in this (dissolved)

form is quickly reduced by the iron to the metallic state—

$$2AgCl + Fe = FeCl_2 + 2Ag,$$

so that there is, so to say, room made in the brine for another installment of silver chloride, which in turn is reduced, and so on. The metal, as soon as freed, is combined with the mercury in a semifluid amalgam, which, on account of its specific gravity, is easily separated from the dross. The silver amalgam is then pressed in linen or some other suitable cloth bags, to separate the amount of comparatively free mercury, which is used again in the process. The remaining solid amalgam is subjected to distillation from iron retorts, the mercury recovered as a distillate, while the silver in a more or less impure state remains in the retort.

The silver furnished by the amalgamating process is never pure, even in a commercial way. A general method of its purification is to fuse it with lead, and subject the alloy to cupellation. Cupel silver is apt to contain small quantities of lead (chiefly), bismuth, antimony, copper, and more or less gold. The first three can be removed by recupellation, without added lead, at a high temperature. The gold, if present to the extent of 1 per cent or more, is removed by treating with nitric or sulphuric acid. The copper is allowed to remain, for commercial silver.

**Argentiferous Galena.**—The lead extracted from galena often contains a sufficient quantity of silver to allow of profitable extraction. This is accomplished by first concentrating the lead and silver alloy by the Pattinson process, which is based upon the fact that the

alloy of silver and lead has a lower fusing point than lead alone, and therefore remains fluid after the purer lead crystallizes. Alloys are thus concentrated from lead containing not more than 3 or 4 ounces of silver per ton to that which contains about 300 ounces to the ton, when by cupellation the lead and other oxidizable metals are removed as oxides, leaving pure silver.

**Desilvering Lead.**—The process is thus described by Bloxam:

"Eight or ten cast iron pots, set in brickwork, each capable of holding about six tons of lead, are placed in a row with a fire placed underneath each of them. Suppose that there are ten pots numbered consecutively, that on the extreme left of the workmen being No. 1, and that on the extreme right No. 10. About 6 tons of the lead containing silver are melted in pot No. 5, the metal skimmed, and the fire raked out from beneath, so that the pot may gradually cool, its liquid contents being constantly agitated with a long iron stirrer. As the crystals of lead form, they are well drained in a perforated ladle (about ten inches wide and five inches deep) and transferred to pot No. 4. When about four-fifths of the metal has thus been removed in the crystals, the portion still remaining liquid, which retains the silver, is ladled into pot No. 6, and the pot No. 5, which is now empty, is charged with fresh argentiferous lead, to be treated in the same manner.

"When pots Nos. 4 and 6 have received, respectively, a sufficient quantity of the crystals of lead and of the liquid part rich in silver, their contents are subjected to a perfectly similar process, the crystals of lead being always passed to the left and the rich argentiferous alloy to the right. As a final result to these operations,

the pot No. 10, to the extreme right, becomes filled with a rich alloy of lead and silver, sometimes containing three hundred ounces of silver to the ton, while pot No. 1, to the extreme left, contains lead in which there is not more than one-half an ounce of silver to the ton."

**Cupellation.**—The extraction of the silver from the rich alloy of silver and lead is accomplished by a process of refining or cupellation, which is based upon the property possessed by certain oxides of being absorbed

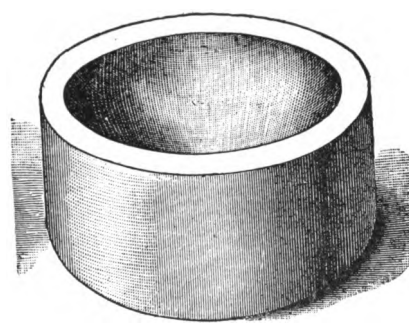


Fig. 47.

by the porous cupel. The process is necessarily modified according to the quantity of alloy to be cupellated; the principle, however, remains identical.

The cupel, Fig. 47, a small, shallow crucible, so named from the diminutive of the Latin *cupa,* a cup, is made from prepared bone-ash, moistened with sufficient warm water to hold it together. Sometimes a little wood-ashes or potassium carbonate is added to the water for moistening the bone-ash. After proper moistening and mixing the cupel is formed by packing and tamping

the moistened ash into a steel mold made for the purpose, and the cupel knocked out by a gentle tap. The ash should not be too fine or packed too densely, or the cupel will lack porosity; nor should it be too coarse or too loosely packed, resulting in a cupel so porous as to cause a loss of the metal. A good cupel, well dried, should not crack on being heated, and should be capable of absorbing nearly its own weight in lead oxide.

The furnace used in operations of a small character is a muffle furnace, called an assayer's furnace, similar to a continuous-gum furnace. The muffle contained is identical with that employed for continuous-gum work, except that a narrow slit is provided on each side or at the end, for the circulation of a current of air over the cupel.

The cupel is first heated in the muffle to an even temperature with the latter, which should be a full red heat. The weighed mass of alloy may then be gently placed on the cupel, the muffle closed, and the alloy heated to redness as soon as possible. When this degree is attained, the muffle is opened and air admitted. As the air strikes the molten mass, a film of oxide quickly makes its appearance upon its surface, which, waving over the melted alloy, is quickly absorbed by the cupel, only to be replaced by other oxide, which is also absorbed; this is continued, the metallic globule rapidly diminishing in size until at last all of the lead has been reduced to an oxide and got rid of. The operator must carefully watch the process during this time, for if the mass becomes too highly heated, silver will be lost by volatilization, and if insufficient heat is maintained, the mass *freezes,* and the proper temperature can not be restored without loss of noble metal. A

proper temperature is maintained by observing the color of the muffle and cupel, the former of which should be reddish-white, and the latter full red, the molten alloy will then appear luminous and clear, and fumes of oxide will be seen whirling over the mass. When the last of the lead has been oxidized and got rid of, the metallic globule remaining is observed to rapidly revolve on its axis, is covered with iridescent tints, and later assumes an exceedingly bright appearance, which is technically termed *brightening* or *coruscation* of the button. When this is observed, the temperature should be somewhat increased to insure the expulsion of the last traces of lead. When the operator is assured that all the lead has been expelled, the button is allowed to slowly cool to prevent **spitting,* sputtering** or *vegetation* of the mass, resulting in a loss of some of the silver. Removing the lead, however, is not the only action; if it were, little would be gained in the process. Another action goes on while the lead is being oxidized in a current of air, and other metals, except gold and silver, are also oxidized and carried off with the litharge. If the lead is therefore properly proportioned, the resulting button will consist of silver and gold, if the latter was present originally. Any gold present may be recovered by the *parting* process. (See chapter on Gold.)

**CHEMICALLY PURE SILVER** in small quantities may be easily prepared in the laboratory by dissolving commercial or coin silver in pure dilute (50 per cent) nitric acid contained in a Florence flask, hastening the action by gently heating over a sand bath. After the

*The O is dissolved as atomic O or as $Ag_2O$, which dissociates at about 1000° C. into Ag and O, which escapes and causes the "spitting."

silver has been dissolved, and the solution somewhat cooled, add an equal bulk of distilled water, and filter into a second flask. To the filtrate add a saturated solution of sodium chloride (common salt) until no more white precipitate of silver chloride is formed—

$$AgN0_3 + NaCl = AgCl + NaNO_3.$$

The flask should then be stopped and shaken for several minutes, when, on being allowed to rest, the chloride will quickly fall to the bottom, leaving a clear, supernatant liquid above, which, if copper be present, will be colored a bluish-green. If to this clear supernatant liquid the salt solution be added, the operator is enabled to determine instantly whether all of the silver has been thrown down as the chloride or not. If so, the clear liquid is decanted off and the chloride washed until the wash-water does not assume the slightest tinge of blue upon the addition of ammonia. The chloride is now best transferred to a beaker, or some other wide-mouthed vessel, and about twice its bulk of water, acidulated with about 10 per cent of sulphuric acid, added. Several small pieces of iron in some form, preferably lath-nails, may now be added to the mixture, and the whole stirred with the closed end of a test tube. The following reactions then take place, during which ferrous sulphate and hydrochloric acid are formed and silver liberated, thus—

$$Fe + H_2SO_4 = FeSO_4 + H_2, \text{ and}$$
$$2H + 2AgCl = 2HCl + 2Ag.$$

The completion of the reaction is recognized by the changing of the precipitated mass from white to a dark

gray, which is the color of the finely divided silver. The small pieces of iron are now removed, the precipitated silver washed and rewashed with dilute hydrochloric acid, then with distilled water, dried, mixed with about an equal bulk of potassium carbonate, and melted in a well-boraxed crucible.

**Pure Silver Nitrate Crystals*** or **pure Silver** may be prepared by digesting commercial, or coin silver, in nitric acid, as before, and evaporating the solution over a sand bath. After the water and free acid is driven off, a greenish solid of silver and copper nitrates remains. By continued heat the former is fused and the latter is changed to black oxide of copper, CuO, by driving off the nitrogen tetroxide (or dioxide, at high temperatures, $NO_2$). When the evaporating dish has sufficiently cooled to be handled, a small quantity of distilled water is added and the contents of the dish stirred and then filtered; the soluble nitrate of silver passes through as a filtrate, leaving the insoluble black cupric oxide on the filter paper. If the preparation of pure silver nitrate crystals is the object of the experiment, evaporate the filtrate to crystallization. If the desire is to recover the silver, this may be done by the addition of sodium chloride to the nitrate solution as before, or by immersing a clean strip of copper in the solution, when the silver will be precipitated upon the copper. Silver obtained in this manner, however, is seldom entirely free from contamination with copper.

*$AgNO_3$, 96 parts, and HCl, 4 parts, when fused yields "lunar caustic." $AgNO_3$, 1 part, and $KNO_3$, 2 parts by weight, when fused yields diluted silver nitrate or "mitigated caustic." Silver nitrate in the presence of sunlight stains organic substances a dark brown color which is difficult to remove after the color change has occurred. If silver nitrate (crystals or solution) come in contact with the skin, discoloration may be prevented by the immediate application of tincture of iodine followed by a solution of hyposulphite of soda.

**PROPERTIES.**—Silver is the whitest of metals, very brilliant, tenacious, malleable and ductile, in the last two qualities being inferior only to gold; if considered weight for weight, it is superior to gold, for while one grain of gold may be beaten so thin as to cover an area of 75 square inches, a grain of silver may be made to cover 98 square inches, though the foil of the former is much thinner than that of the latter. The extent of the malleability of gold and silver has never been absolutely determined, as the means employed have invariably failed before the property in either was exhausted. In tenacity silver is superior to gold. It is also harder than gold, but softer than copper, and is the best known conductor of heat and electricity. It fuses at 961.5° C., far below the fusing point of either gold or copper. It volatilizes appreciably at full red heat; in the oxyhydrogen flame it boils, with the formation of a blue vapor. The fused metal readily absorbs oxygen gas (when fused under potassium nitrate it takes up as much as twenty times its volume.) As the metal cools, the oxygen, escaping through the semi-solid crust on the surface of the fused mass, produces very beautiful effects. Pure silver retains a trace of the absorbed oxygen permanently. It is unaltered in the air at any temperature, but is readily acted upon by sulphur, phosphorous, or chlorine.

**COMPOUNDS WITH OXYGEN.**—There are three oxides of silver, only one of which ($Ag_2O$), however, can be regarded as a well-defined compound.

The **Monoxide,** or *Argentic Oxide,* $Ag_2O$, is a strong base, yielding salts isomorphous with those of the alkali metals. It is obtained as a pale-brown precipitate on adding caustic potash to a solution of silver

nitrate. Very soluble in ammonia, and slightly so in pure water, forming an alkaline solution. It is easily decomposed by heat; the sun's rays also effect a slight decomposition, as is the case in most compounds of silver.

The other two oxides are the **Argentous Oxide,** $Ag_4O$, and **Silver Dioxide,** $Ag_2O_2$.

**ACTION OF ACIDS ON SILVER.—Nitric Acid** is the proper solvent for silver, and is most efficient when diluted about 50 per cent, but active whether concentrated or dilute, with production of nitric oxide ($N_2O_5$) and silver nitrate ($AgNO_3$).

**Sulphuric Acid** hot and concentrated, acts upon silver, forming a sulphate which is sparingly soluble.

**Hydrochloric Acid,** hot and concentrated, forms argentic chloride, slightly soluble in the concentrated reagent, but precipitated on dilution.

Fused **alkaline hydrates** or niter are without action upon silver; hence, it is used for the manufacture of crucibles for the fusion of caustic alkalies, etc.

**ALLOYS.**—Pure silver is too soft for coinage or commercial purposes, and for casting because it absorbs oxygen, which is given off on cooling, producing a cauliflower-like appearance, or the oxygen may be retained as bubbles. It is, therefore, alloyed variously for its different purposes to increase its hardness.

**Gold.**—Formerly silver was much used to alloy gold. The metals are easily mixed together, but do not appear to form definite compounds. With certain proportions of the metals the resulting alloys are more ductile, harder, more sonorous and elastic than either metal considered singly. While the tensile strength is in-

creased, up to 50 per cent of the alloy, silver hardly lowers the fusing point of gold. An alloy of Au. 40, Ag 60, requires more than 1050° C. to fuse, whereas the melting point of gold is 1060° C.

**Copper.**—The alloys of copper and silver are the most useful of the alloys of silver. In most countries the silver coins are made of these two metals. In the United States the silver for coinage is alloyed with 10 per cent copper, the proportion of each being stated in the thousandths; thus, pure silver being 1000 fine, the coin or "standard silver" is 900 fine, with 100 parts of copper added. The German and French silver coins are of the same grade, those of Great Britain are 925 fine, with 75 parts of copper added, being known as "sterling" silver. Most silverware is of "sterling" fineness. The presence of copper does not modify the color of silver so long as the proportion of the former does not exceed 40 or 50 per cent. Copper imparts to silver greater hardness, tenacity and strength, Ag 80, Cu 20 giving maximum degree.

Comparison of the silver dollar of the United States with that of Mexico:

| | U. S. Dollar | Mexican Dollar |
|---|---|---|
| Pure Silver ..... | 371.25 grs. | 377.14 grs. |
| " Copper ..... | 41.25 " | 40.65 " |
| Total weight.... | 412.50 " | 417.79 " |

The Mexican dollar contains 5.89 grains more silver than the United States dollar, and .60 grains less copper. It is also 5.29 grains greater in weight than the United States dollar.

The Mexican dollar is equal to 0.866 of a Troy ounce.

**Zinc** and silver have a great affinity for each other, and are consequently readily alloyed.

Silver solder for soldering the metal is usually composed of an alloy with copper and zinc. The following are well adapted for the purpose:

| No. 1* | | No. 2† | |
|---|---|---|---|
| Silver | 66 parts | Silver | 6 parts |
| Copper | 30 " | Copper | 2 " |
| Zinc | 10 " | Brass | 1 " |

When the material to be united is composed of pure silver and platinum, silver coin alloyed with one-tenth zinc may be used as a solder.

So-called standard silver is also an excellent solder for high fusing brass and German silver. If the article is to be soldered twice, this may be used first and the silver solder afterwards.‡

Dr. Kirk§ recommends the following compositions:

| Fine Silver | Copper | Brass | Zinc |
|---|---|---|---|
| 4. | .... | 3. | .... |
| 2. | .... | 1. | .... |
| 19. | 1. | 10. | 5. |
| 66.7 | 23.3 | .... | 10. |
| 50. | 33.4 | 16.6 | .... |
| 11. | .... | 4. | 1. |

These may be used for soldering the surfaces of standard silver.

**TESTS FOR SILVER IN SOLUTION.—Hydrochloric acid** and the soluble **chlorides** precipitate *silver chloride,* AgCl. It is a white, curdy substance, quite insoluble in water, and nitric acid; one part of silver

*Richardson, Mechanical Dentistry, p. 78.
†Ibid.
‡Professor C. L. Goddard.
§Am. System of Dentistry, iii, p. 879.

chloride is soluble in 200 parts of hydrochloric acid, when concentrated. When heated, it melts, and on cooling it becomes a grayish, crystalline mass, which cuts like horn. It is found native in this condition, constituting the mineral called *horn-silver*. Silver chloride is decomposed by light, turning violet to brown (forming argentous chloride, $Ag_2Cl$) both in the dry and in the wet state, very slowly if pure, and quickly if organic matter be present. It is reduced also when put in water with metallic zinc or iron. It dissolves very readily in ammonia and in a solution of potassium cyanide. This precipitation is the most delicate of the ordinary tests for silver, being recognized in solution in 250,000 parts of water.

**Potassium and sodium hydrate** precipitate from solutions of silver salts, *silver oxide,* $Ag_2O$, grayish brown, insoluble in excess of the reagents, easily soluble in nitric, acetic, or sulphuric acid, and in ammonia.

**Sulphuretted hydrogen** throws down a black precipitate of silver sulphide.

**Potassium chromate** gives a red precipitate of silver chromate, $Ag_2CrO_4$, which is soluble in ammonia, and concentrated nitric acid.

**ELECTRODEPOSITION OF SILVER.**—Silver is the most important and prominent metal in electroplating processes.

The solution generally used is the cyanide, and it may be prepared by either of two methods—the battery or the chemical process.

The method of procedure in the former is simple, when thoroughly understood. First must be ascertained the percentage of actual cyanide in the salt

used. If, say, it contains about 50 per cent, dissolve each ounce in about one quart of distilled water; or if it contains more, add more water, and vice versa in proportion. Suspend a large anode and a small cathode of silver in the liquid, and pass a strong current of electricity through, until the required amount of metal is dissolved from the anode. As this process produces some caustic potash in the liquid, some of the strongest hydrocyanic acid may now be added to form cyanide, and more of the anode dissolved in the mixture aided by the battery.

Making solutions for deposits by the chemical process is accomplished as follows:

Take four parts of pure grain silver, and reduce it by mixing with nitric acid to argentum nitrate. Dissolve this in distilled water, in the proportion of one quart to every one-half ounce of silver used. At the same time make a solution of from two to three parts of cyanide of potassium in twenty or thirty parts of distilled water. This is to be added gradually to the solution of nitrate of silver as long as it produces a white precipitate. If too much be added, however, it will cause some of the precipitate to be redissolved and wasted. In such a case the liquid should be stirred and then allowed to settle clear. A small amount of nitrate of silver dissolved in distilled water should be added as long as it produces a white cloud. This may be better conducted by using a glass vessel and observing the precipitate as it dissolves. The liquid should now be left to settle until quite clear, and the clear portion then decanted, and the precipitate washed four or five times in a large quantity of water by simply adding the water, stirring and allowing it to settle

again and decanting as before. Next dissolve from six to eight parts of cyanide of potassium in twenty parts of distilled water, adding it, a portion at a time, with free-stirring, to the wet cyanide of silver, until the whole is barely dissolved; then add about three parts more of cyanide of potassium to form free cyanide, and sufficient distilled water to reduce the whole to the proportion of about one-quarter of an ounce of silver to the quart; finally, when all the free cyanide is dissolved, filter the solution and it is ready for use. The specific gravity of the solution should be maintained at between 1.8 and 1.15.

Deposit solutions are very numerous, but in the author's judgment, the above is best adapted for a good, reguline solid deposit.

Knowledge of the management of solutions is essential. There are varying circumstances which must be noted in order to keep them in good condition for a reguline deposit. New solutions do not work as well, usually, as old ones, provided the latter is not too old. Solutions two or three years old work probably the best. They change from many causes; they become dirty and concentrated from exposure; increase or decrease in their relative proportions of cyanide and metal; they acquire other metals in solution, dissolved from the anode and corroded from the cathode; plaster and plumbago accumulate in them, and in consequence of which they should be filtered; they gradually decompose, become brown, discolored, and evolve ammonia by exposure to light, especially if they contain too much free cyanide; therefore, all these deviations from the proper condition should be corrected. The specific gravity should be maintained, and the proper

amount of metal and cyanide kept in solution. To determine any disproportion in the latter, place 25 grams of the solution in a test tube of proper size and add to it, at first freely, and afterwards gradually, until at last, drop by drop, with constant stirring, a solution of one gram of crystallized nitrate of silver in ten grams of distilled water. If the precipitate formed is dissolved rapidly, with but little need of stirring, there is too much cyanide. If, however, it does not dissolve, even after much stirring, there is too little cyanide; but if it wholly dissolves (the latter part quite slowly) the proportion of silver to cyanide is about correct.

Many other minor troubles not mentioned are encountered, which must be corrected by means gathered only from experience in working the process.

The process for making dental bases by electrodeposition on the plaster cast of the mouth was patented February 5, 1889, by Joseph G. Ward, of Irvington, N. J.

The author has had some experience in the work; in fact, was engaged in perfecting a process for the same result when Mr. Ward secured his patent. The method of proceeding in the preparation of a dental base is as follows:

A true impression of the mouth is secured, and from this a cast is obtained by filling in the usual manner. After the cast has become thoroughly dry it should be soaked in hot fluid paraffine until saturated, and before cooling the surface wiped clean of all superfluous adhesions which might in any way destroy the exactness of the model. The cast is then coated freely where the deposit is desired with a mixture of equal parts of pure finely pulverized plumbago and the finest tin-

bronze powder or any other conducting substance suitable under the circumstance. This is applied with a thick, short-haired camel's-hair pencil. The cast is now so wired that perfect connection is made with the palatine, buccal, and labial surfaces. From these guiding wires a cathode-hook suspends the cast in the solution. After the metal has been deposited to a sufficient thickness, the cast, with its deposit, is to be taken from the bath, the deposit removed from the cast, trimmed and polished; but if it is desired to have the plate of increased thickness at any part to give the appearance of a turned-rim, etc., the cast, with the deposit adhering to it, may be removed from the bath, and all the exposed surface of the deposit, except the portions to be thickened, may be covered with a coating of wax or some other nonconducting substance and resubmerged in the bath and left there until the required thickness of deposit is secured in the parts desired. It may then be taken from the bath, burnished, trimmed by scraping, burring and filing to the proper shape and thickness, then polished, and spurred. A thick plating of gold should now be added to the properly shaped plate, or the rubber for the attachment of the teeth will not harden and adhere to the plate during the process of vulcanization (the sulphur of the vulcanite combining with the silver). After the teeth have been attached and the vulcanite and all properly finished, a second coating of gold should be electroplated over it all to cover portions that had been made bare in finishing the vulcanite.

The denture may be made by depositing the metal directly on the teeth as in cheoplastic work, and, where

necessary, clasps may be formed. Broken dentures have been soldered with 18-carat gold solder.

Crowns and bridge work may also be made in various ways by this process.

Electrolytic methods of refining the rare metals have superseded all others in the United States mints, where the problem is to separate the metals in a pure state from mixtures of all proportions of gold, silver, and base metals. The silver is first brought up to purity and then the gold. The silver rarely runs lower than 99.9% pure. The platinum is recovered by precipitation and is a valuable by-product.

# CHAPTER XVII

## IRIDIUM

| | |
|---|---|
| Iridium. | Symbol, Ir. |
| Valence, II, IV. | Specific gravity, 15.86. |
| Atomic weight, 193.1. | Malleable, at red heat. |
| Melting point, 1950° C. | Chief ore, iridosmine. |
| Color, steel-white. | Crystals, hexagonal. |

**OCCURRENCE.**—The metal occurs chiefly as a native alloy of iridium and osmium, known as *osmiridium* or *iridosmine,* in combination with platinum. The principal source of supply is Russia, where the crude platinum carries from one to three per cent of iridium. The United States produces from 100 to 200 ounces annually. One area in Trinity County, Cal., carries twice as much iridium as platinum in the gravel beds. Other sources of supply are Oregon, Colorado and Columbia, South America.

**REDUCTION.**—It is obtained from its native alloy by mixing with an equal weight of dry sodium chloride, and heating to redness in a glass tube, through which a moist stream of chlorine gas is transmitted. The mixture of iridium and osmium sodio-chlorides thus formed is dissolved in water and evaporated, and distilled with nitric acid, removing the osmium as osmic acid; when its complete removal is thus effected, ammonium chloride is added to the residual solution, which precipitates the ammonio-chloride of iridium as a dark-red-brown precipitate. From this spongy metallic iridium

is obtained in the same manner as the production of spongy platinum.

**PROPERTIES.**—Iridium is a steel-white metal, exceedingly hard, brittle when cold, but somewhat malleable when at red heat, having a specific gravity of 15.86 unaltered in air, and fusible only in the oxyhydrogen flame. If the precipitated metal be moistened with a small quantity of water, pressed tightly between filter paper, and then very forcibly in a press, and calcined at a white heat, it may be obtained in the form of a very hard compact mass, capable of taking a good polish, but still very porous, and having a specific gravity not to exceed 16.

**COMPOUNDS WITH OXYGEN.**—Iridium forms three oxides:

The **Monoxide,** or *Hypoiridious Oxide,* IrO, is but little known, and upon being exposed to the air is quickly converted into a higher oxide.

The **Sesquioxide,** or *Iridious Oxide,* $Ir_2O_3$, may be formed by exposing the metal at a red heat to the action of the oxygen of the air. It is a black powder, insoluble in the acids and much used for imparting an intense black to porcelain.

The **Dioxide,** or *Iridic Oxide,* $IrO_2$, is also a black powder, obtained by heating the tetrahydroxide in a current of $CO_2$. It is insoluble in acids, and is said to be the most stable oxide of the metal.

**ACTION OF ACIDS ON IRIDIUM.**—The *pure metal* itself is *not acted upon* by the acids, but when reduced by hydrogen at a low temperature, it oxidizes slowly at a red heat; and may be dissolved in nitrohydrochloric acid. It is, however, usually rendered soluble by fusing

it with potassium nitrate and caustic potash. Its hydroxides are also soluble. It forms two chlorides, $IrCl_3$ and $IrCl_4$, and analogous iodides, and three sulphides analogous to the three oxides.

**ALLOYS.**—With **Mercury.** Dr. Kirk relates that "Böttger formed an amalgam with iridium by immersing sodium amalgam in an aqueous solution of chloridate of sodium; he describes the amalgam as soft and viscid."

With **Gold** iridium forms a malleable and ductile alloy, its color depending upon the proportions of the metals.

**Platinum** and iridium form some very valuable and useful alloys. Jewelers find such alloys durable and safe for setting diamonds, pearls, and other light colored precious stones. Aside from these, and the use of the metal and its alloy with phosphorous for pointing gold pens, iridium is of little value.

With **Silver** it is claimed there is no alloy; and that after exposing a mixture of these metals to a high temperature, or attempting to pour out the contents of the crucible, silver alone flows out and a thick mass is left in the crucible.

## CHAPTER XVIII

## PALLADIUM—TUNGSTEN

| | |
|---|---|
| Palladium. | Symbol, Pd. |
| Valence, II, IV. | Specific gravity, 11.4-11.9. |
| Atomic weight, 106.7. | Malleability, 11th rank. |
| Melting point, 1546° C. | Chief ore, in gold and platinum. |
| Conductivity (heat), —. | Conductivity (electricity), 12.1. |
| (Silver being 100.) | |
| Specific heat, 0.0592. | Crystals, fibrous. |
| Color, platinum-white. | |

**OCCURRENCE.**—Palladium is found native in company with platinum from which it is distinguishable by its fibrous structure. It is usually found, however, alloyed with platinum and with some specimens of Brazilian gold.

**REDUCTION.**—When the solution of crude platinum from which the greater part of the metal has been precipitated by salammoniac, is neutralized by sodium carbonate, and mixed with a solution of mercuric cyanide, palladium cyanide separates as a whitish insoluble substance, which on being washed, dried, and heated to redness, yields metallic palladium in a spongy state. The palladium may then be welded into a mass in the same manner as platinum.*

**PROPERTIES.**—Palladium is a white metal, much resembling platinum, though somewhat darker in color. Its specific gravity differs greatly from that of platinum, being only 11.4. It is also very much less ductile and malleable than that metal; it is the most fusible of

*Manual of Chemistry, Physical and Inorganic, Watts.

the platinum group, yet it barely melts at the highest wind-furnace heat, or about the temperature at which malleable iron fuses, 1546° C., and when heated to redness and exposed to the air, especially in its spongy state, it acquires a blue or purple superficial film of oxide, but may be restored to its brightness and luster upon being heated to a more intense degree, the oxide being reduced. If heated and fused in air, it is apt to vegetate on cooling, similarly to silver.

The metal is most remarkable for its property of "*occluding*" or *absorbing* hydrogen. According to Graham the compact metal when immersed in *cold* hydrogen gas takes up little or none of it; but at higher temperatures very considerable occlusions take place. A certain specimen of palladium-foil at 245° C. was found to absorb 526 times its own volume of hydrogen; and at red heat will absorb nearly 1,000 volumes. The hydrogen, as in the case of platinum, is retained in the metal on cooling. Graham views hydrogenized palladium as a true alloy, containing its hydrogen in the form of a metal—"hydrogenium." Palladium has not the power of absorbing oxygen or nitrogen. If palladium be used as the negative electrode in the electrolysis of water, the coefficient of absorption is very high; especially is this the case when the palladium was produced electrolytically and hydrogenized while itself in the nascent state. Such metal cold was found to contain 982 volumes of hydrogen, corresponding approximately to the formula $Pd_4H_3$. The element does not lose any of its metallic properties by being hydrogenized, but it loses nearly 10 per cent of its specific gravity. At the same time its bulk is increased about one-tenth.

**DENTAL APPLICATIONS.**—Formerly palladium was used to some extent as a base for artificial dentures. Its lightness (having little more than half the specific gravity of gold), hardness, and resistance to discoloring and corroding influences made it desirable. Scarcity prevents its present use.

**COMPOUNDS WITH OXYGEN.—Palladious Oxide,** the *Monoxide,* PdO, may be prepared by evaporating to dryness and cautiously heating the solution of palladium in nitric acid. It is of black color, but slightly soluble in acids, and decomposed by high temperature.

**Palladic Oxide,** the *Dioxide,* $PdO_2$, is not known in the separate state. From palladic chloride solutions alkalies and their carbonates throw down a brown precipitate, hydrated palladic oxide combined with the alkali. The hydroxide is decomposed by high heat; dissolves slowly in acids, forming yellow solutions.

**ACTION OF ACIDS ON PALLADIUM.**—In **Hydrochloric** or **Sulphuric Acid** boiling and concentrated palladium is slightly soluble, forming palladious chloride, $PdCl_2$, or palladious sulphate, $PdSO_4$.

**Nitric acid** dissolves it slowly, but it is more readily soluble in a mixture of nitric and nitrous acids, forming palladic nitrate, $Pd(NO_3)_4$.

**Nitrohydrochloric acid** is a ready solvent for this metal, forming palladic chloride, $PdCl_4$. The solution is a deep brown color, decomposed upon evaporation with a liberation of chlorine and becoming $PdCl_2$.

**ALLOYS.**—With Mercury, in the finely divided state, it readily combines to form a gray plastic amalgam. This union is attended with the evolution of some heat, and is said to result in a definite chemical compound. (See chapter on Amalgams.)

Palladium renders its alloys harder and more brittle. These are chiefly used in the manufacture of fine watches, and the most important are those with silver and the so-called palladium bearing-metal.

In the laboratories of the Research Institute of the National Dental Association, experiments have been made with many metals which might possibly serve as a substitute for platinum.* Of all the alloys experimented with, the palladium-gold group presented the best results. The authors state that "the remarkable property of palladium from a metallurgic point of view is its great solvent power for other elements, forming solid solutions in perhaps more cases than any single element. These two metals alloy readily in any proportion. The alloy is insoluble in hydrochloric acid and aqua regia, slightly soluble in sulphuric acid, and soluble with difficulty in nitric acid. It may be rolled into very thin sheets and used as a substitute for platinum foil. One per cent of palladium changes the color of gold to a light yellow, two to three per cent gives a bronze color, and five per cent approaches the color of palladium. It was found that this alloy will "solder as well as pure gold."

**Silver.**—An alloy of palladium 9 parts and silver 1 part was used for dental bases, as was also the following: platinum 10, palladium 8, and gold 6 parts. Mr. Fletcher says * * * a silver alloy poor in palladium is worthless, as a large amount of the latter is necessary to protect it from sulphuretted hydrogen. And, further, that pure palladium is the best metal known for plates for artificial teeth, owing to its high

*Weston A. Price and F. A. Fahrenwald: Metallurgical, Physical, and Chemical Researches, Jour. N .D. A., i, No. 4, 71-109.

specific heat, its extreme lightness and hardness, requiring no alloy, and also to its absolute freedom from tarnish.

The same author further says: "As an alloy, the presence of palladium in small quantities is frequently objectionable, * * * almost inadmissible, even in so small a proportion as 1 to 2000 in silver for making amalgams."

Price and Fahrenwald found that "palladium increases the hardness of silver in the alloy without adding value to its tensile strength or workability." "It therefore offers no special values as a substitute for platinum and iridium alloys."

With **nickel** it forms a malleable alloy susceptible to high polish.

With **antimony, bismuth, tin, zinc, iron,** and **lead** it combines to form very brittle alloys.

**Palladium bearing-metal.**—An uncommonly hard alloy used as bearings for fine watches, and is said to produce less friction upon arbors of hard steel than the jewels generally used. The composition is, palladium 24, gold 72, silver 44, and copper 92.

**TESTS FOR PALLADIUM IN SOLUTION.**—Salts of palladium may be discriminated by:—

**Sulphuretted hydrogen** or **ammonium hydrosulphide,** which throws down a black precipitate of palladious sulphide, insoluble in alkaline sulphides, but soluble in hydrochloric acid.

**Potassium iodide** gives a black precipitate of palladium iodide from palladious chloride.

**Potassa** or **soda** yields a red precipitate soluble in excess of alkali if heated.

**Mercuric cyanide,** the characteristic test, gives a yellowish-white gelatinous precipitate of palladious cyanide from solutions of palladious chloride, which is soluble in hydrochloric acid.

Nearly all the compounds of palladium are reduced by heat, before the *blowpipe,* to a "sponge." If this be held in the inner flame of an alcoholic lamp it absorbs carbon at a heat below redness; if then removed from the flame, it glows vividly in the air, till the carbon is all burnt away—(distinction from platinum).

**TUNGSTEN,** until recently a rare metal, has been developed into a very valuable one. It occurs generally in the presence of manganese and tin ores and for a long time was considered a constituent of cassiterite. It is prepared by heating pure tungstic oxide in an atmosphere of hydrogen, in the form of briquets, 0.5x0.5x15. cm., sintering at about 1300° C. until the oxide is reduced. These briquets are then heated electrically to about the melting point of tungsten and then subjected to repeated swagings to weld into a solid compact mass. It is then drawn through diamond and ruby draw-plates, first hot and then cold, until the size of wire needed is obtained.

The symbol is W., named wolfram on account of its causing the loss of tin in smelting in the same sense that antimony was called "the wolf" by the alchemists because it devoured the base metals when employed in refining gold. It has an atomic weight of 184.0, a specific gravity of 18.81, and a melting point of 3002° C. It is both brittle and ductile, depending on the manner of working it. The acids have only a slight action on it, usually forming tungstic oxide

which prevents further action. The alkali carbonates and a saturated solution of hypochlorite attack it appreciably.

It is used and most commonly known as the metallic filament in electric lamps. The U. S. Dept. of Mines has estimated that if tungsten filament lamps were substitued for carbon filament lamps, an annual saving of $250,000,000 would be effected. It is also used for targets in roentgen tubes, for electric furnaces where an atmosphere of hydrogen or nitrogen can be maintained, for standard weights, and for filtering acid liquors. It is paramagnetic and very elastic and therefore suitable for watch springs. It is extensively used as a constituent in lathe tool-steel, since it has the property of retaining its temper at red heat, and is known as self-hardening steel. It is curious that the old Damascus steel has been found to contain both chromium and tungsten. Colorado, U. S., and Australia are the largest producers.

F. A. Fahrenwald* in endeavoring to find a dependable substitute for platinum in dentistry, has produced tungsten wires coated with gold and palladium. They are designed to serve as dowels for crowns, and for orthodontic appliances. As yet they have not fulfilled all the exacting requirements for this service in a practical way. An effort was also made to produce an alloy of gold and tungsten, by mixing gold chloride and tungstic oxide in varying proportions, placing the compound in a quartz tube electric furnace, and reducing to a metallic state in the absence of oxygen. A very fragile alloy was the result, no matter what combination was used.

*F. A. Fahrenwald: A Development of Practical Substitutes for Platinum, etc., Jour. N. D. A., iii, pp. 47-84.

# CHAPTER XIX

## PLATINUM

| | |
|---|---|
| Platinum. | Symbol, Pt. |
| Valence, II, IV. | Specific gravity, 21.48 at 17.6°. |
| Atomic weight, 195.2. | Malleability, 6th rank. |
| Melting point, 1753° C. | |
| Ductility, 3d rank. | Tenacity, 3d rank. |
| Conductivity (heat), 16.64. | Conductivity (electricity), 14.4. |
| (Silver being 100.) | |
| Specific heat, 0.0323. | Chief ore, polyxene. |
| Color, bluish silver-white. | Crystals, octahedral. |

**OCCURRENCE.**—The ore of platinum *"polyxene,"* which is a most complex mixture of a number of heavy reguline species of platinum, osmiridium, iron-platinum, platin-iridium, iridium, palladium, gold, and a number of nonmetallic species, notably chrome-iron ore, magnetic iron oxide, zircone, corundum, and occasionally also diamond, is found in the province of Choco, South America, where it was first discovered in 1736, in New Granada, Barbacos, California, and Australia, but chiefly in alluvial deposits in the Ural district. The variable percentages of the several components range approximately as follows: Platinum, 60 to 87; other polyxene metals, 3 to 7; gold, 2 and more; iron, 4 to 12; copper, 0 to 4; nonmetallic gangue, 1 to 3. Gold is separated by amalgamation when it exists in any considerable quantities.

Platinum is rarely found in large nuggets, but usually in granules, which are generally small, but occasionally assume considerable dimensions. The Demidoff Mu-

seum contains a native platinum lump weighing 21 pounds troy.

**REDUCTION.**—The extraction of platinum is accomplished by two distinct methods. The first, devised by Wollaston, which produces the purest metal, is more of a chemical than a metallurgic process, a modification of the method of Heræus is as follows: The ore is digested within glass retorts in dilute aqua regia, by which the platinum, palladium, part of the iridium, and more or less of the other metals pass into solution, the platinum, palladium, and iridium as tetrachlorides. The solution is then evaporated to dryness, and the residue heated to 125° C., to reduce the palladic and iridic chlorides to the lower stages of $PdCl_2$ and $Ir_2Cl_6$, which form soluble double salts with ammonium chloride. The heated residue is dissolved in water acidulated with hydrochloric acid; the solution filtered and mixed with a hot concentrated solution of ammonium chloride, when a quite pure chloroplatinate, $PtCl_6(H_4N)_2$, comes down in a yellow precipitate, which is washed first with a saturated ammonium chloride solution, then with hydrochloric acid. This precipitate needs only to be exposed to a dull red heat to be converted into "spongy platinum," that is, metallic platinum in the form of a gray, porous mass. Care must be taken that no gold chloride in combination with ammonia remains since it is violently explosive and the application of heat may do serious damage.

The second method, known as Deville's, is based upon the tendency of platinum to be dissolved in melted lead. The ore is fused with an equal weight of galena (sulphide of lead) and as much of the oxide of lead. The sulphur and oxygen escape as sulphur

dioxide, the reduced lead dissolving the platinum, and leaving the very heavy alloy of osmium and iridium to sink to the bottom undissolved. The upper portion containing the platinum is then ladled out and cupellated, (see chapter on Silver), when the latter metal is left in a spongy mass, the lead having passed off as the oxide.

**FUSING PLATINUM.**—Modern practice in the fusion of platinum does not differ materially from previous methods. An ordinary sand crucible, with one side knocked out may be used, but a block of freshly calcined lime, obtained from magnesia limestone, free from silicon, iron, and aluminum is better than straight calcium limestone. It should be wrapped with wire to prevent cracking, and placed on a block of magnesite or some other refractory substance to prevent loss of heat. An oblong or rectangular trough is cut in the lime to facilitate handling the button or ingot. An oxyhydrogen flame, or gasoxygen flame with a specially constructed burner is used, for the gas usually comes under a pressure of less than a pound, while the oxygen is under great pressure. A pressure regulator must be attached to the oxygen tank. The flames should not be sooty as the carbon may contaminate the metal. The scrap should not be massed but stacked up against the side of the crucible and the flame directed below gradually fusing the lower portion and allowing the upper portion to melt in.

When the ingot is cool enough to handle, it should be inverted on a soldering block and the flame directed against the surface to fuse the roughened surface, thus getting rid of the pits and siliceous substances that may be attached. This is called sweating. One part of silicon in 3000 parts of metal will render the latter

brittle. When the mass melts in two layers and does not fuse in the crucible, is swaged and separates in two layers, or blisters, it is called "double platinum." Remelting will correct this condition. In the case of platinum sponge the mass is introduced before heating up the furnace, and it is here that the furnace acts as a cupel; the impurities remaining in the metal are oxidized and volatilized or absorbed by the lime of the furnace. The temperature produced is supposed to be about 2870° C. Osmium does not melt at this point but if present is volatilized with palladium and gold.

Platinum may also be fused by placing the metal between the carbon tips of an arc light.

**PROPERTIES.**—The metal is bluish silver-white, about as soft as pure copper, and has a specific gravity of 21.48. It is tough, ductile, and malleable, and may be rolled or beaten into foil or drawn into wire of almost microscopic fineness. Dr. Arendt states* that a cylinder of platinum, one inch in diameter and five inches long, may be drawn into a wire sufficiently long to encircle the earth at the equator. The fine wire used in micrometer eye-piece of microscopes suggested by Wollaston is made by drawing a composite wire of platinum, coated with silver, to its greatest attenuation, and then dissolving off the silver in nitric acid. Platinum possesses **tenacity** in a high degree, being slightly inferior to iron and copper. The fusing point, according to Violle is 1753° C. When heated much above its fusing point, it soon begins to volatilize. The fused metal, like silver, absorbs oxygen, and consequently spits on freezing. At a red heat it occludes

*Dr. Kirk in American System of Dentistry, iii, p. 887, from Anorganischen Chemie.

hydrogen gas. The volume of hydrogen absorbed by a unit volume of metal at a red heat, under one atmosphere's pressure, was found, in the case of the fused metal, to vary from 0.13 to 0.21, volumes measured cold; in the case of merely welded metal from 2.34 to 3.8 volumes. Oxygen, though absorbed by the liquid, is not occluded by the solid metal at any temperature, but when brought in contact with it at moderate temperatures, suffers considerable condensation at its surface, and in such a state exhibits a high degree of chemical affinity. When a jet of hydrogen gas strikes a layer of spongy platinum it causes it to glow and the gas takes fire.

The most striking example of the property of the metal for absorbing gases is demonstrated in the finely divided state known as "platinum black." This state is produced by dropping platinum chloride solution into a boiling mixture of 3 parts of glycerine and 2 of caustic potash. Platinum black is said to absorb 800 times its volume of oxygen from the air, and is, therefore, a most active oxidizing agent, acting catalytically, that is, after having given up its oxygen to the oxidizable substance it takes up a fresh supply from the atmosphere.

**DENTAL APPLICATIONS.**—About one-third of the world's total production of platinum is used in dentistry, and from the nature of its use it is recovered in only small amounts. The metal has become so valuable in science and industry where the recovery is large that the Federal Government has proposed measures looking toward the conservation of the supply and the substitution of other metals for jewelry and dental purposes.

Dentists should welcome any effort made to provide suitable substitutes and encourage research looking to that end.* Platinum was introduced in France as early as 1820 for a base in continuous-gum work. Its low rate of expansibility under increased temperature, its coefficient being about equal to that of glass, and its very high fusing point make it most useful for porcelain work, and for pins for artificial teeth. Its comparatively great resistance to chemical agents insures it against corrosive action, and places it on an equality with gold for dental bases, crowns, and bridge-work.

Platinum and gold is used as a filling material in the form of platinum and gold folds, platinized gold folds, and platinum and gold foil. The color of this material inserted as a filling is not as beautiful as that of either gold or platinum alone. The yellow of gold having almost entirely disappeared leaves an ashen effect to the platinum, which very much detracts from its characteristic color and appearance. The advantage it possesses over gold is its tough, resistant property—making a surface that will stand the abrasive action of mastication much better than gold.

Coils of platinum are much used in the construction of muffles for electric furnaces and in various forms of electric heating devices. The heat is free from products of combustion and can be most accurately controlled. A device of this nature is especially valuable in annealing gold.

**COMPOUNDS WITH OXYGEN.**—Platinum forms two compounds with oxygen.

**Platinous Oxide,** or *Monoxide,* PtO, is obtained by

*See footnote, p. 283.

digesting the platinous chloride with caustic potash as a black powder, soluble in excess of the alkali. It is not known in the separate state, is a feeble base, and is decomposed by heat, leaving metallic platinum.

**Platinic Oxide,** or *Dioxide,* $PtO_2$, also a weak base, occasionally acting as an acid; hence, it is sometimes termed platinic acid. It is best prepared by adding barium nitrate to a solution of platinic sulphate; barium sulphate and platinic nitrate are thus formed, and from the latter caustic soda precipitates one-half of the platinum as *platinic hydroxide.* The hydroxide is a bulky brown powder which, when gently heated, becomes black and anhydrous. If this oxide be dissolved in dilute sulphuric acid and the solution mixed with an excess of ammonia, a black precipitate or fulminating (explosive) platinum is obtained, which detonates violently at about 190° C.

**ACTION OF ACIDS ON PLATINUM.**—The metal is not sensibly tarnished by sulphuretted hydrogen vapor or solution; and is not attacked at any temperature by nitric, hydrochloric or sulphuric acid; but it dissolves in nitrohydrochloric acid to form platinic chloride. It is, however, less readily soluble in this acid than gold.

**ALLOYS.**—Platinum alloys with most of the metals. With **mercury** spongy platinum unites to form an exceedingly unctious amalgam. It does not, however, unite readily, and its union is best accomplished by continuous rubbing in a warm mortar.

**Iridium** from 10 to 15 per cent added to platinum greatly increases its hardness, elasticity, infusibility, electrical resistance, and resistance to chemical action. Platinum alloyed with iridium can be made very use-

ful in dentistry as dowels, etc., and to strengthen weak parts of partial continuous-gum and partial vulcanite dentures and crown and bridge-work. An alloy of 78.7 platinum and 21.3 iridium will withstand the action of aqua regia. An alloy of iridium 5-20 parts and platinum 95-80 parts is used as a thermocouple in electrical pyrometers. Equal parts of the metals form a very brittle alloy.

**Gold** and platinum form an alloy of great value for the construction of dental bases. Platinum gives to gold a greater hardness and elasticity. Two parts to one of gold forms a brittle alloy, while with equal parts the alloy is malleable. Dr. Weston A. Price recommends an alloy of platinum, 6 parts, and gold, 94 parts, for casting, upon which porcelain can be baked. Dr. George L. Bean recommends adding scrap platinum foil to coin gold, in proportions to suit the operator's judgment, for casting plates and bridges. Gold 75 parts and platinum 25 parts forms an alloy much used in continuous gum and porcelain crown and bridge-work. It is usually called 25 per cent platinum solder.

**Silver.**—By small additions of platinum to silver its pure white color is changed to a gray, and its hardness is increased. The alloys are difficult to make, on account of the separation of the platinum, owing to its greater specific gravity.

**Platine au titre,** an alloy composed of from 65 to 83 per cent of silver, has been used for dental bases in preference to coin silver, on account of its resistance to chemical action and its greater elasticity. Nitric acid will dissolve an alloy of silver and platinum when the latter is not present, to exceed 10 per cent.

**Cadmium** and platinum unite, to form a definite compound, having the formula of $PtCd_2$.

**Copper** and platinum, equal parts, form a gold-colored alloy tarnishing in air.

**Iron**; reinforced platinum protected by U. S. patents, is made by taking a metal of the iron group, encasing it in a tube of platinum, and heating it to welding heat when union takes place. It may be made by casting superheated ferrous alloys against platinum. Spun ware from this double faced platinum is thus produced.

**Lead and tin** unite with platinum in all proportions, resulting in hard and brittle alloys with comparatively low fusing points. Pure platinum should never be brought in contact with these or other low fusing metals or their alloys at high temperatures, as alloys of platinum having a low fusing point and brittle character are readily formed.*

**TESTS FOR PLATINUM IN SOLUTION.—Sulphuretted hydrogen** throws down, after heating, a blackish brown precipitate.

**Potassium** or **ammonium hydrate** each throws down a very characteristic yellow crystalline precipitate, the former soluble in large excess of precipitant, and the latter, when dried and heated, yielding metallic platinum.

By the reducing *blowpipe* flame, the compounds of platinum are reduced to spongy platinum.

*Organic or other salts of lead, bismuth and antimony should not be heated on platinum, for the metals may be reduced and form fusible alloys with the platinum.

## CHAPTER XX

## GOLD

| | |
|---|---|
| Aurum. | Symbol, Au. |
| Valence, I, III. | Specific gravity, 19.32. |
| Atomic weight, 197.2. | Malleability, 1st rank. |
| Melting point, 1060° C. | Tenacity, 5th rank. |
| Ductility, 1st rank. | Chief ore, found native. |
| Conductivity (heat), 70.03. | Conductivity (electricity), 76.6. |
| (Silver being 100.) | |
| Specific heat, 0.0316. | Crystals, octahedral. |
| Color, yellow. | |

**OCCURRENCE.**—Gold is found in nature chiefly in the metallic state, or as native gold, and less frequently in combination with tellurium, lead, and silver. It is also found combined, or, perhaps, more strictly speaking, minutely mixed with pyrites and other sulphides, more commonly called "sulphurettes."

**Native gold** occurs rather frequently in crystals belonging to the cubic system, the octahedron being the commonest form, but other and complex combinations have been observed. Large crystals are rarely well defined, owing to the softness of the metal, the points being commonly rounded. The most characteristic forms, however, are the *nuggets* or *pepites.* These, when of weight less than one-quarter to one-half an ounce, are known as *gold dust.*

Except the larger nuggets, which are usually more or less angular or irregular, gold is generally found in a bean-shaped or somewhat flattened form, the smallest particles being scales of scarcely appreciable

thickness, and owing to their small bulk, as compared with their surface, they are frequently suspended in water and may be washed away by rapid current; hence, they are known as *float gold.*

In the museum of the Mining Bureau in San Francisco are several plaster of Paris models of famous gold nuggets found in the various gold regions of the world. The largest single piece of gold ever found was taken out at Ballarat, Victoria, Australia. It weighed 2166 troy ounces, and was valued at $41,882. The second largest was discovered in the Ural Mountains district, and weighed 1200 ounces. The third largest, which was also found in Victoria, Australia, weighed 1121 ounces, and was valued at $22,000.

The physical properties of native gold are quite similar to those of the melted metal and its alloys. The composition varies considerably in different localities as shown in table on page 298.

The most important minerals containing gold are:

**Sylvanite,** or graphic tellurium, $(AgAu)Te_2$ containing 24 to 26 per cent.

**Calaverite,** $AuTe_2$, containing 42 per cent. The calaverite, a nearly pure telluride of gold, has been found to some considerable extent in Calaveras County, California. Hence the name of the county.

**Nagyagite,** or foliate tellurium, of a complex and rather indefinite composition, and containing from 5 to 9 per cent only of gold.

The minerals of the second class, called *auriferous,* are comparatively numerous, and include many of the metallic sulphides. The most important of these are iron pyrites and galena; the first of these is of great

ANALYSIS OF NATIVE GOLD FROM VARIOUS LOCALITIES

| Locality | Gold | Silver | Iron | Copper |
|---|---|---|---|---|
| EUROPE: | | | | |
| British Isles— | | | | |
| Vigra and Clogau..... | 90.16 | 9.26 | Trace | Trace |
| Wicklow (River) ..... | 92.32 | 6.17 | .78 | .... |
| Transylvania ..... | 60.49 | 38.74 | .... | 0.77 |
| ASIA: | | | | |
| Russian Empire— | | | | |
| Brezovsk ..... | 91.88 | 8.03 | Trace | .09 |
| Ekaterinburg ..... | 98.96 | 0.16 | .05 | .35 |
| AFRICA: | | | | |
| Ashantee ..... | 90.05 | 9.94 | .... | .... |
| AMERICA: | | | | |
| Brazil ..... | 94.00 | 5.85 | .... | .... |
| Central America ..... | 88.05 | 11.96 | .... | .... |
| Titiribi ..... | 76.41 | 23.12 | .... | 0.87 |
| California ..... | 90.12 | 9.01 | .... | .... |
| Mariposa ..... | 81.00 | 18.70 | .... | .... |
| Caribou ..... | 84.25 | 14.90 | .... | .03 |
| AUSTRALIA: | | | | |
| South Australia ..... | 87.78 | 6.07 | 6.15 | .... |
| Ballarat ..... | 99.25 | 0.65 | .... | .... |

practical importance, being found in many districts exceedingly rich, and, next to the native metal, is the most prolific source of gold.

**A Native Amalgam** of gold is found in California, but rarely in any considerable quantities.

Gold is so widely distributed throughout the earth's crust that few regions may be said to be destitute of slight traces of it; yet it has been found in comparatively few localities in quantities sufficient for economic extraction. The principal supplies of the metal have

been derived from Africa, California, Nevada, Alaska, Australia, Mexico, Brazil, Ural Mountains, Transylvania, etc.

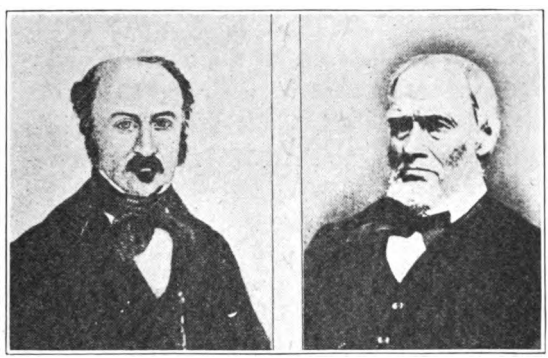


Fig. 48.—James W. Marshall, who discovered gold in California in January, 1848, and John A. Sutton, who financed the expedition.

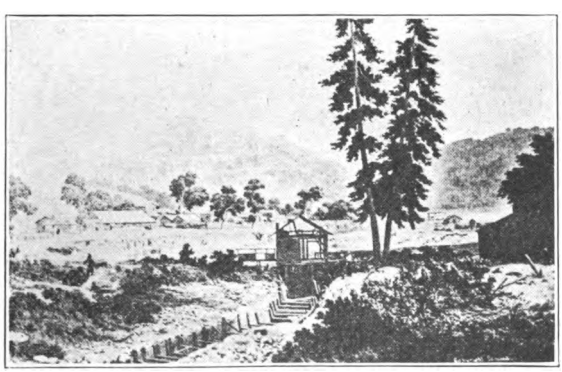


Fig. 49.—The "tail race" at Sutter's Mill, California, where gold was discovered by John W. Marshall.

California was for many years chiefly known to the world as the region where gold was found in extra-

ordinarily large quantities. Great excitement was occasioned by the discovery of the precious metal in January, 1848, and its subsequent extraction from the *placers* of the Sierra Nevada Mountains. The gold regions of California are the mountain counties lying between Shasta and Lassen on the north, and Fresno on the south. At the time of their greatest productiveness the yield reached about $65,000,000 in value a year, this was from 1850 to 1853.

Fig. 50.—A California prospector in early days.

The association and distribution of gold may be considered under two different heads; namely, as it occurs in mineral veins, and in alluvial or other superficial deposits which are derived from the waste or disintegration of the former. As regards the first, it is usually found in quartz veins or reefs traversing slaty or crystalline rocks either alone or associated with such metals as iron, copper, tellurium, and rarely bismuth, or such minerals as magnetic and arsenical pyrites,

galena, specular iron ore, and silver ore, and rarely with the sulphides of molybdenum, tungstate of calcium, bismuth, and tellurium minerals.

In the second or alluvial class (placers) of deposits it is associated chiefly with those minerals of great density and hardness, such as platinum, osmiridium, and other metals of the platinum group, tinstone, chromic, magnetic, and brown iron ores, diamond, sapphire, ruby, topaz, etc., which represent the more dur-

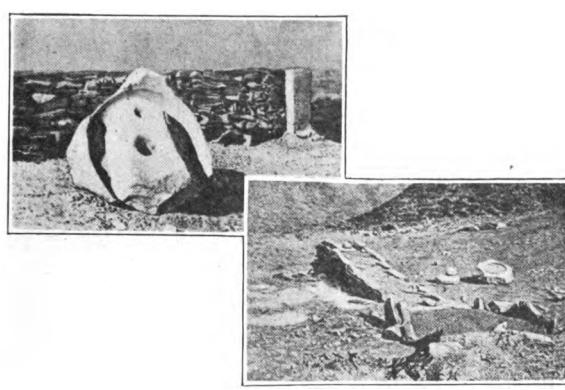


Fig. 51.—Ancient gold mining in the Sudan. The milling or crushing of the ore was done in stone grists, the nether stone being hard and about 20 inches in diameter. The mullers were of a softer coarse grained granite. The quartz was fed through the hole in the top and the rocking or grinding effected by means of a short stick in the smaller hole on the side. The washing table in the lower picture is much like the modern sluice.

able original constituents of the rocks whose disintegration has furnished the detritus.

**MINING AND EXTRACTION.**—It is believed that gold has reached the maximum of production. There are very few localities in Siberia, South America and Africa which have not been fully explored. In the future the increase in production must come from more

intensive working and a closer saving. The simplest and oldest form of mining and extracting the precious metal is known as—

**Placer mining,** which consists of washing the alluvial deposits, sands of rivers, and other earthy matter, by which the lighter particles of earth and sand are

Fig. 52.—Panning gold.

washed away, while the gold in irregular and flattened grains by its gravity remains.

In the early days of California, when rich alluvial deposits were common at the surface, the simplest appliances sufficed, the most characteristic of which was—

*The "pan,"* a circular dish of sheet-iron, with sloping sides about 13 or 14 inches in diameter. The pan, about

two-thirds filled with *pay dirt* to be washed, is held in a stream or in a pool of water. The large stones separated by hand; the pan is given a twisting lateral motion, keeping the contents suspended in the stream to remove the lighter substances, the heavier gold remaining on the bottom. This process is termed *panning out.*

*The "cradle"* is a simple contrivance based upon the

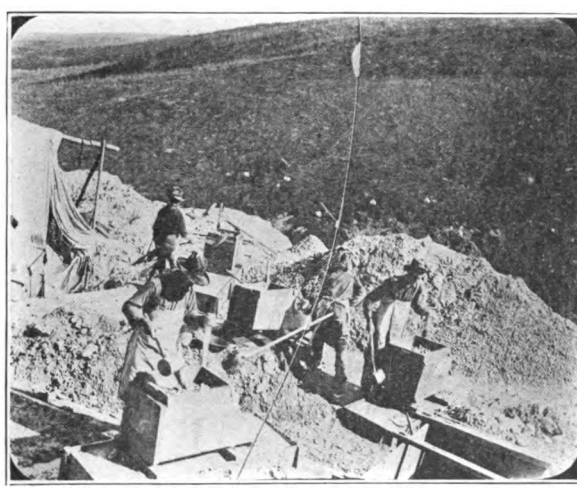


Fig. 53.—The "cradle" in use in the Alaskan gold fields.

same principle for treating somewhat larger quantities.

*The "tom"* is a sort of cradle with an extended *sluice* placed on an incline. Under certain circumstances mercury is used in the sluice to amalgamate the gold.

*The "sluice,"* a Californian invention, is used in working on a larger scale, where the supply of water is abundant. The simplest form of this consists of a rectangular trough of boards set up on trestles at an in-

clination that the stream of water may carry off all but the largest stones, which are kept back by a grating, and removed by hand as they accumulate. The floor of the sluice is provided with *riffles* made of strips of wood laid parallel with the current, and at other points with boards having transverse notches filled with mer-

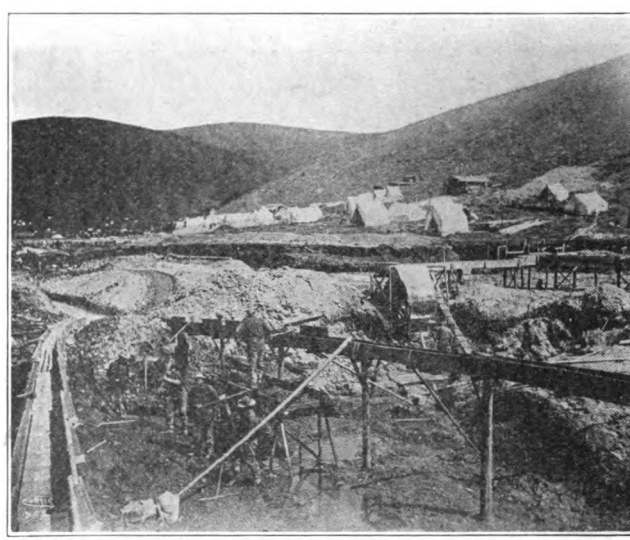
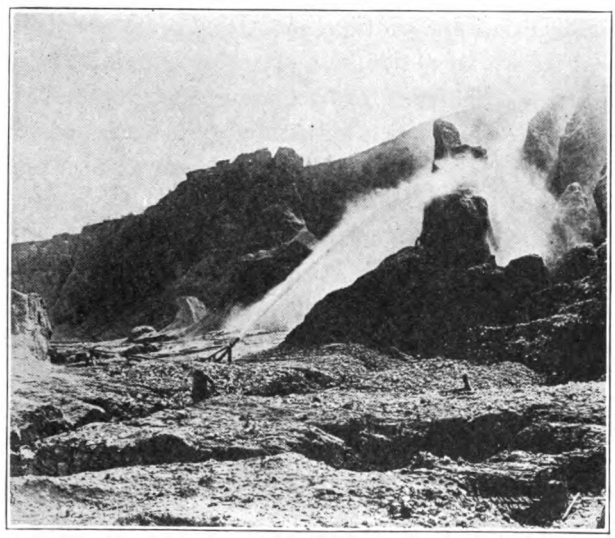


Fig. 54.—Sluicing gold in Alaska. Water is oftentimes very difficult to obtain in some fields and then it is used over and over again.

cury for the accumulation of the gold. The length of the sluice depends, of course, upon the volume and flow of water, the ordinary ones ranging from 100 to 500, and even to 1000 feet in length, while the sluices leading from hydraulic operations are sometimes a mile in length.

**Hydraulic Mining.**—This method is also a Californian



Figs. 55 and 56.—Two views of hydraulic operations; the first shows the mortar at work tearing down the soil, while the second shows the big sluices into which all the detritus flows.

invention, and has for the most part been confined to the placer mining of this State. The method is employed where an abundance of water is available, and where thick banks of auriferous gravel are to be removed; it consists in loosening and washing away banks of gravel, sand, and soil with powerful streams of water discharged from nozzles resembling those of a fire hose. It is supplemented by the use of gunpowder for breaking up and removing "bed rock," immense boulders, etc., and arrangements must be made for saving the gold without interrupting the flow of water, and for disposing of the vast masses of impoverished gravel. The stream from the site of operation laden with stones and gravel passes into sluices where the gold is recovered in the manner already described.

**Quartz mining** does not greatly differ from the methods employed in the extraction of similar deposits of other metals. The quartz is first reduced to a very fine powder; this is accomplished in the most productive regions, such as California and Australia, by means of the *stamp mill.* In this operation cylindrical iron pestles, weighing from 600 to 800 pounds, are lifted by means of cams, and allowed to fall some 8 or 10 inches at the rate of from 30 to 90 blows per minute upon the quartz. A stream of water carries the comminuted material into contact with mercury, which, on account of its great affinity for the gold, absorbs and separates it from the earthy gangue. To prevent the "sickening" and "flouring" of the mercury, which is produced by certain associated minerals in the ore, and which occasions much annoyance and some considerable loss of both gold and mercury, by greatly dimin-

ishing the solvent powers of the latter metal, a small quantity of the amalgam of sodium is added to the mercury.

Before the mercury becomes saturated it is removed and subjected to powerful pressure in leather bags,

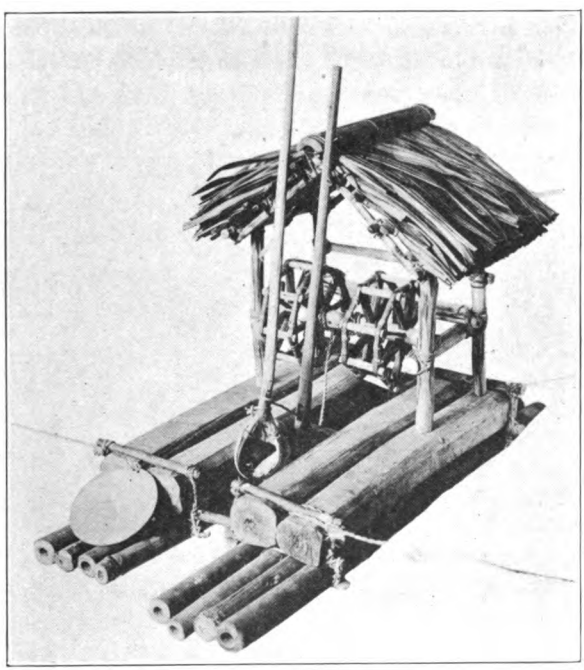


Fig. 57.—A primitive Philippine dredger operated by hand on the interior rivers.

when the excess is squeezed out through the pores of the leather leaving the more or less coherent mass of rich amalgam inside. The mass is then heated in a proper vessel, when the mercury is distilled over and recondensed in iron retorts. The gold is left in a

spongy state usually quite free from other metals, except silver, which is separated by the "parting process," to be subsequently described. The spongy gold with its silver content is then melted in plumbago crucibles with the addition of a small quantity of suitable fluxes and shipped as bullion.

In some cases it has been found advantageous to smelt the ore by fusing it with lead, which latter in the fused state has a very great affinity for gold. In such

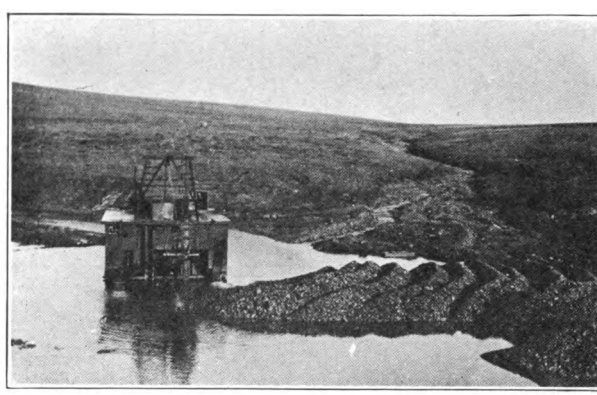


Fig. 58.—A huge dredger operating in one of the rivers in the Alaskan fields. During the summer months the machinery is in operation twenty-four hours in the day with no need for electricity for illumination.

operations the crushed ore is mixed with suitable proportions of metallic lead or litharge and charcoal, together with some lime or clay as a flux for the silica and fused on the hearth of a reverberatory furnace. The melted lead dissolves the particles of gold, just as mercury does, and sinking beneath the lighter slag, is drawn off and afterward separated from the gold by cupellation.

**DREDGER MINING.**—Dredger mining differs from other methods only with respect to the manner of obtaining the ore. Usually a mining claim is selected in a valley where the debris from the surrounding mountainous country has been accumulating for countless centuries, and where the hard pan or bed rock is not more than forty feet below the surface of the soil.

It makes no difference whether the claim is on an arid portion of the land or in a river bed if water to float the dredger can be obtained. A large excavation is made and filled with water; the dredger is launched and operations begin. The earth is removed by a series of buckets on an endless chain, each bucket having a capacity of 1000 pounds or more. The lips of the buckets are constructed of manganese steel and are thus capable of withstanding heavy stresses in scooping up the earth. Usually they engage about six inches of the hard pan or bed rock for most of the gold is found there, and then every bit of earth is taken up to the surface. The water in the excavation tends to soften the earth and is also used on the washing tables. The earth is carried to a large revolving separator which separates the large rock from the clay and finer earth, the latter passing over the jig table if no pulverizing is necessary. From there the ore is washed over the amalgamators where the gold is collected for further refining.

**Chlorination Process.**—Under some circumstances it is found best to separate the gold from the quartz in a wet way by means of chlorine. The process depends upon the fact that chlorine acts rapidly upon gold, but does not attack ferric oxide, and is now adopted in Grass Valley, California, where the waste minerals prin-

cipally pyrites, have been worked for a considerable time by amalgamation.

The ore is roasted at a low temperature in a reverberatory furnace, during which salt is added to convert all the metals present, except iron, into chlorides. The auric chloride is, however, decomposed, at the elevated temperature, and the finely divided particles are readily attacked by the chlorine gas. The roasted mineral, slightly moistened, is then introduced into a wooden vat which is provided with a double bottom. Chlorine gas is led from a generator beneath the false bottom, and rises through the moistened ore, converting the gold into a soluble chloride which is afterwards removed by washing with water. The noble metal is then precipitated by the sulphate of iron. The method is very accurate and yields metal of great purity.

**FLOTATION PROCESS.**—See chapter on compounds of metals and nonmetals, p. 53.

**CYANIDE PROCESS.**—This process has been developed to increase the production of precious metals, gold and silver, by a greater recovery, and is based upon the solubility of these metals and some of their mineral compounds in an alkaline cyanide solution. Elsner's theory of the action of oxygen in the dissolution of precious metals first showed the possibilities of this method of reduction. The equation showing the reaction is as follows:

$$2Au + 4KCN + O + H_2O = 2KAu(CN)_2 + 2KOH.$$

The ore is first crushed to free the native metal, if gold, or the gold and silver compounds from the gangue, and is mixed with water to form a slime. In certain

instances where the ore requires a long contact with the cyanide solution to dissolve it, the crushing is not carried to so great a degree of fineness, merely producing a coarse sand, and the minerals or metals are leached out.

Formerly potassium cyanide was used, but now cyanides of sodium and calcium are used, chiefly for economy. The calcium cyanide is converted into calcium hydroxide which is sufficiently soluble to keep the solution alkaline, while the suspended particles are carried away with the tailings. The essential difference between gold and silver cyaniding is that gold usually occurs native while silver is found principally as the sulphide, chloride, or bromide. The concentration of the cyanide solution as well as the time of treatment and the comminution of the ore are important factors which must be determined at the plant.

Certain minerals or portions of the gangue may act as cyanicides and destroy the value of the solution as a metal solvent. These ores may require some preliminary or accessory treatment, though all gold and silver ores are capable of recovery by this process. Usually the slimes are allowed to stand in contact with the solvent for twenty-four hours, when the solution is drawn off and the metal precipitated electrolytically, or by zinc shavings. The recovery is so complete in some instances that the loss does not exceed one and one-half grains per ton.

The strength of the cyanide solution varies from 0.5 to 0.3 per cent, or from 0.1 lb. to 5-6 lbs. per ton of ore. On such a basis the cost is less expensive than smelting. At Cerro de Pasco, Peru, there is a bed of tailings esti-

mated at 15,000,000 tons, which is being worked by the cyanide process for the recovery of silver at a profit, and ultimate returns are estimated at $30,000,000.

**REFINING GOLD.**—Unless it can be utilized, the accumulation of gold in the form of scraps, filings, etc., in the dental laboratory and operating-room frequently becomes a source of considerable loss to the dentist, because he is unfamiliar with the methods of refining, or lacks the necessary apparatus.

Some forms of scrap gold, such as old fillings, need only to be melted with the proportion of silver, copper, or both, to produce the desired alloy. Others, as scrap plate of known carat, may be utilized for casting bridge pontics, cusps for crowns, etc.

Old crowns, plates, bridges, mixed fillings containing more or less iron from the file, zinc, lead, antimony, and other base metals, may be converted into malleable gold by simply roasting with such fluxes as will combine chemically with the base metals and remove them.

Sweepings may be washed and then carried through the same process, which is known as

**THE ROASTING PROCESS.**—A method for roughly refining and rendering brittle gold malleable. This process may be most satisfactorily employed where the approximate carat of the bulk of the scraps is known and the gold is suspected to be unworkable, owing to the admixture of base metals.

The larger pieces should be removed from the accumulation and the smaller ones with the filings freed from as much iron and steel as possible by a good magnet. All should then be placed in a previously well-boraxed and tried graphite crucible, with the addition

of sufficient potassium carbonate to well cover the charge; the object of this addition being to form, when heated, a thin flux, permitting the small particles and filings to sink and accumulate in one mass.

The furnace should be placed beneath a fume-chimney or by a window with an outward draught, that the fumes escaping from it during the roasting may not fill the laboratory, thereby endangering the health of the students or operator and damaging such instruments and tools as may be unprotected. The most convenient place to avoid such results is the fire-place. The furnace may be placed beneath its chimney in such a manner that all fumes will be readily carried off.

When the metal has become thoroughly fused, the refining process may be begun, by first adding small quantities of the oxidizing agent, potassium nitrate, ($KNO_3$), accompanied with borax as needed to properly protect the mass and further the process. The object of the potassium nitrate is to furnish sufficient oxygen to oxidize the contaminating base metals beneath the flux, thus separating them from the gold. As most base metals are easily oxidized under these circumstances, a continuation of this process from ten minutes to one hour and a half, according to the quantity of material, and the proportion of base metals contained, adding the nitrate and borax as required, and maintaining a state of perfect fusion of the metal, the ingot, when made by pouring into a previously warmed and oiled mold, will be found to be quite malleable.

If, however, upon examination it is found to be still brittle, it should be placed in a clean, boraxed, and tried crucible, heated, and brought to a perfect state of fusion. A mixture of equal parts of finely pulver-

ized vegetable charcoal and ammonium chloride should then be added; at first sufficient to properly cover and protect the molten mass, and afterwards a small quantity at a time as it is needed. When the metal has been sufficiently treated, which may be determined by removing small quantities and subjecting them to the physical tests for malleability, the crucible is to be removed from the furnace and the metal cast into an ingot or allowed to cool in the crucible as a button.

The *rationale* of such a process is that the heat of the crucible breaks up the chloride compound, liberating the chlorine in the nascent state; which in turn combines with the metals lead, tin, and silver, contained in the gold to form their respective chlorides. These are either volatilized or taken up by the flux, and the gold remains free of them.

Mercuric chloride is sometimes used when the contamination of the gold with lead or tin is extensive, or where it is desired to remove a quantity of silver. But its use is so dangerous on account of the fumes evolved that it is rarely employed.

Sulphur or antimonic sulphide is used to abstract large quantities of silver from gold, by combining with the former to form fusible sulphide of silver, leaving the gold free, or if the antimonic sulphide has been used, contaminated with antimony, which may be removed by fusing with borax and potassium nitrate, as previously described.

In the process of refining by fluxes, the first step should be to determine, as far as possible, the nature of the debasing elements; this being known or reasonably approximated, the process may be confined to the particular flux most likely to free the gold from its con-

tamination. Iron, steel, zinc, copper, antimony, and bismuth are, perhaps, best removed by oxidation, through the agency of potassium nitrate. Lead, tin, and silver are removed by chlorine.

If, after such treatment, the alloy is found to be malleable, but stiff or elastic, or dull in color, it very probably contains some platinum which can not be removed by this means, but which may be got rid of by a *wet method.* When desired, such an alloy may be made direct use of as clasp gold.

When the object is to produce pure gold from which to subsequently prepare desired carats by alloying the results, it is best and most conveniently attained by the process known as

**PARTING GOLD.**—A wet method for refining gold by inquartation, or "quartation," as it is more commonly called. This is accomplished by digesting the thinly rolled or granulated alloy of silver and gold in either nitric or sulphuric acid.

The student, in his choice of metal for this operation, may endeavor to obtain gold containing as much silver as possible, and, as this will require an additional quantity of the latter metal fused with it in order to carry out the operation, it is of course an object, if possible, to employ silver which contains small quantities of gold, and thus, as it may be said, to carry on a double refining process at once.

As the actual separation of the two is effected by digesting the mixture in hot nitric acid, which, while it is a ready solvent for other metals, is inactive upon gold, it may be asked: Why not at once treat the alloy with acid without such alloying? Such would be quite useless, for, the foreign metals being in so small a

relative proportion, the acid would only remove the alloy at or near the surface, the metal being sufficiently close in texture to mask all the rest from the action of the acid.

The sulphuric acid process is doubly recommended, especially when large quantities of the alloy are to be digested, as it is less expensive, and the gold is obtained of a greater degree of fineness. The oxidizing action of the nitric acid is of especial value, however, when tin or antimony is present in the batch of metal.

**Preparation of the alloy.**—The impure gold is first weighed and the approximate weight of the silver, if it contains any, subtracted; silver is then added in the proportion of three to one, less the amount already contained in the alloy, thus when melted forming an alloy of three parts silver and one part impure gold. Hence the term "quartation." These proportions are then fused together in a clean and boraxed crucible, well mixed, and either poured into warmed and oiled ingot molds, to be subsequently rolled, or dropped while molten from the crucible into a wooden tub or tank of cold water for the purpose of granulation. The latter is unquestionably the simplest method of preparing it for digesting process, for, if poured into the ingot molds, the alloy will require rolling to a very thin ribbon (No. 35 gauge), after which it must be cut into small pieces. The rolling many times is impossible, because of the gold that it is desired to refine being exceedingly brittle. The alloy being thus prepared, is ready for the acid.

**Nitric Acid Process.**—For this process the prepared alloy is placed in a Florence flask and nitric acid to the amount of about one and one-half times the weight of

the alloy poured on. The acid should always be tested for chlorine by adding a drop of the solution of silver nitrate ($AgNO_3$) to it, which, if chlorine be present, will instantly be rendered milky from the precipitated chloride of silver. Heat the flask gently in a sand-bath over a Bunsen or alcohol flame. Copious red fumes of the oxides of nitrogen and ammonium will be given off, showing vigorous action on the alloy, and the silver and other metals will be dissolved, leaving the gold in a spongy mass of a blackish-brown color. When this evolution has entirely ceased and the flask is clear, carefully decant the solution of the nitrates of silver, etc., thus formed and preserve it, adding a fresh portion of nitric acid and boil until all fumes cease to rise, which marks the termination of the digesting process. The acid is now replaced by distilled water two or three times, for the purpose of washing the gold remaining. At length filter the contents of the flask, catching the gold on the filter paper, add a sufficient quantity of potassium carbonate, fold the paper over the whole, and place in a previously boraxed crucible, melt and pour into warmed and oiled ingot molds.

Gold thus refined may reach .998 fineness, and is ready for any desirable alloying.

For the recovery of the silver, see chapter on that subject.

**Sulphuric Acid Process.**—The use of sulphuric acid for the operation is preferred by many. For, as was stated, it is more economical; and the gold so refined is more thoroughly freed from silver; indeed, it is said that gold having been previously refined by the means of nitric acid may be freed of still more silver by this acid. In operating the metals are so mixed that the

gold amounts, at most, to not quite half the weight of the silver; and if copper is contained, (which in small proportions facilitates the operation), it should be under 10 per cent, for, if too much be present, a large quantity of sulphate of copper will be formed, which latter is insoluble in the strong acid liquors. The process may be employed for silver containing very small quantities of gold. Thus, in France, it was found very profitable to separate the gold from old five-franc pieces, which contained only .001 to .002 of gold.

The alloy having been granulated, as before described is introduced into a digester (Florence flask) with about two and one-half times its weight of concentrated sulphuric acid. This is allowed to boil, during which strong action is evidenced by copious evolution of sulphur dioxide, while the silver and copper are simultaneously converted into sulphates. This first boiling is continued as long as sulphur dioxide is evolved, which in large quantities of metal will commonly go on about four hours. The liquid is then removed and a smaller quantity of acid added, the boiling being further carried on for a short time, after which the digester is allowed to remain at rest, in order that the gold may subside. Sometimes it may be requisite to use even a third acid.

Repeated washing of the gold with boiling water is now necessary, as the sulphate of silver is a very insoluble salt, and sulphate of copper, when contained in so acid a menstruum, is also somewhat so. The gold is then dried, melted, and poured, as described before.

This process affords gold as pure as .9985.

**THE PREPARATION OF CHEMICALLY PURE GOLD.**—The metal, either in the form of powders, granulations, thin plate, or "cornets" from the purest gold that can be obtained, is dissolved in chemically pure nitrohydrochloric acid. The best material to operate on is gold which has been refined in the ordinary way; this may be used in the form of a powder, as it is precipitated in the last process, as granulations or as plate. The acid for small quantities is best contained in an evaporating dish placed in a sand-bath upon a tripod, over the flame of a Bunsen burner, beneath a chimney or near an open window. The action will be tolerably energetic when the metal is first introduced; hence, it is not necessary to ignite the burner at the start, but as the action slackens a moderate heat may be applied.

Normal aqua regia consists of $HNO_3 + 4HCl$, but for dissolving gold the acid should be prepared by mixing 200 c.c. HCl (density 1.19), 45 c.c. $HNO_3$ (density 1.4), and 245 c.c. $H_2O$, which are the proportions recommended by Prat in 1870. Gold dissolves in aqua regia in accordance with the equation $Au + HNO_3 + 4HCl = 2\ H_2O$ and $NO + HAuCl_4$, and any excess of either acid is unnecessary.

Each ounce of gold will require about three and one-half ounces of mixed acid for its solution. During the process of solution a sediment will be noticed in the bottom of the evaporating dish, which will be recognized by the operator as a silver chloride, formed by the union of the silver contained in the gold and the liberated chlorine. It must not be expected that all the silver will be directly precipitated to the bottom as a chloride, for the liquor is strongly acid, and some may

be held in solution. Therefore, this must be taken into consideration, and subsequent pains taken to throw it down by the thorough evaporation of the nitric acid. The gold having been dissolved, the solution is now best transferred to a clean dish by decantation, leaving the chloride of silver in the first and the solution contained in the second dish heated to further evaporate. When about one-third is evaporated more chloride of silver will be found to have been separated from the solution and precipitated. It is well, therefore, to again transfer the solution to a third dish by decantation and evaporate as before, care always being maintained during the heating not to apply so great a temperature as to decompose the auric salt which adheres to the side of the dish above the fluid.

As the bulk is reduced over the gentle heat by evaporation, small quantities of hydrochloric acid are to be added from time to time, which has the effect of liberating nitrous anhydride by decomposing the remaining nitric acid in the liquor; these additions must, however, be made very cautiously, for the action produced is very energetic, and without due precaution, considerable portions of the now rich liquor will be spurted out of the dish and lost. When the liquor has become of a deep red color, and of the consistency of syrup, it is to be withdrawn from the heat and permitted to rest for a time, when the whole of the auric chloride will crystallize, forming a mass of prismatic crystals.

The bottom of the dish is now carefully wiped off to remove any sand or dirt that may have collected there from the sand-bath, and the dish and its contents immersed in about a half pint of *distilled water,* acidulated slightly with hydrochloric acid. It is better now

to let this solution stand a week, for chloride of silver, although slightly soluble in a very strong and hot acid solution, is separated by dilution, and, by allowing this rest, it will completely subside in the vessel. At the end of this time the solution must be filtered to remove any foreign substance, together with the silver chloride. The filtrate will then be seen to be a rich straw-yellow, and the gold it contains is ready for precipitation.

**Precipitating the Gold.**—The solution is now best contained in a large glass flask, and the precipitating reagent added. As gold is one of those metals which, as a base, combines with very feeble affinities, it is consequently not only very easily separated, but the physical conditions of the precipitate may be much modified and controlled by the nature of the precipitant, as also by the mode of operating. Thus the gold may be thrown down in a powder, in scales, in more or less of a crystalline state, in a tolerably compact sheet or foil, or lastly, in a spongy condition much resembling so-called "solila" or "moss fiber." And these states may be attained with some degree of certainty, although the circumstances determining the more compact forms are hardly yet well understood.

Spontaneous precipitation may take place to some extent in a vessel of trichloride of gold when exposed to the air; and thus the sides of the vessel containing it will slowly become covered with the deposit. This is probably due to the action of the nitrogen of the air. Many elementary substances will precipitate gold from the trichloride. Most of the lower metals will reduce it, some metallic salts throw it down, and many organic bodies readily precipitate it. Thus sugar when boiled

in it gives at first a light red precipitate, which afterwards darkens in color.

Practically, however, ferrous sulphate or oxalic acid are the only precipitants used. The oxalic acid is preferred, and is an excellent precipitant.

The gold salt, being in solution, is broken up by the addition of a strong solution of oxalic acid, and the gold is precipitated to the bottom as either a crystalline mass or a leafy foil. It is necessary to add a slight excess, and the whole should be kept at a gentle heat in a sand-bath over a flame. Soon after the application of heat some slight bubbling is noticed, a copious evolution of gas takes place, and at the same time the body of the liquid appears filled with most delicate spangles of metallic gold, which become coherent as they descend, and in consequence assume most any one of the forms above mentioned. The gas noticed to escape is $CO_2$, from the compound, oxalic acid. The reaction is of the simplest—an acid on a binary salt—

$$2AuCl_3 + 3C_2H_2O_4 = 6HCl + 6CO_2 + 2Au.$$

The action of this precipitant being gradual, and capable of much regulation, by the amount and nature of heat employed, while it is also peculiar in being attended throughout by this evolution of gas which rises quickly through the solution, there is produced from the former cause a tendency in the metal to deposit in a crystalline or crystallo-granular state; while from the latter a more or less spongy character is given to it; hence it will be readily seen that inasmuch as we are able to modify these conditions, so we can in the same degree influence the molecular nature of the result.

Where ferrous sulphate is used, about four times

the weight of the gold will be necessary for precipitation. This may be dissolved quickly in hot distilled water and added to the gold solution. The precipitate thrown down is of a brown color, and will, on being gently burnished with the finger-nail, assume that metallic golden luster characteristic of the metal. The following is the reaction—

$$2AuCl_3 + 6FeSO_4 = Fe_2Cl_6 + 2Fe_2(SO_4)_3 + 2Au.$$

After the solution has fully subsided from the disturbance caused by addition and precipitation a quantity of hot hydrochloric acid may be added, and much of the supernatant liquor removed, either with a siphon or by decantation, and the remainder of the solution and precipitate poured upon the filter paper. The precipitate is afterwards washed with hydrochloric acid, distilled water, aqua ammonia, and again with distilled water. The necessity of this is apparent, especially in the use of ferrous sulphate as the precipitate will become more or less contaminated with the iron, and in the use of oxalic acid this is to remove the copper, as gold precipitated by oxalic acid from an acid solution containing copper is always contaminated with cupric oxalate. It is then also advisable to heat the solution with a slight addition of potassium carbonate, a soluble double oxalate of copper and potassium is formed, and the gold is left in the pure state. Gold may also be precipitated from its acid solution in a state of purity in the form of brilliant spangles by means of hydrogen dioxide,* thus—

*The precipitation of gold is very slow in an acid solution. In the presence of $LiCO_3$ it is complete in a few hours, and more rapid with $K_2CO_3$. Wash well with dilute HCl after precipitating.

$$2AuCl_3 + 3H_2O_2 = 6HCl + 6O + 2Au.$$

When the precipitated gold has been carefully washed and rewashed with distilled water, and the above-mentioned reagents, it may be dried and placed in a new crucible, previously boraxed, with some potassium carbonate and potassium nitrate melted and cast into an ingot. If iron ingot molds are used the gold should be washed after molding in hot hydrochloric acid to remove any trace of metallic or oxide of iron that may by chance have adhered to its surface during the process of casting the ingot.

**PROPERTIES.**—Pure gold is a rich, beautiful yellow color, of strong metallic luster, unalterable in air. It is the most ductile of all metals, but ranks only fifth in point of tenacity. One grain, however, if covered with a more tenacious metal, like silver, forming a composite wire, may be drawn into a wire 550 feet in length, and only 1/5000 of an inch in diameter. It is also the most malleable of all metals. One grain of it may be beaten into leaves so thin as to cover an area of 75 square inches, being of but 1/370,000 of an inch in thickness.

Very thin leaves of gold appear green in color by transmitted light, but when heated, the light transmitted is ruby-red.

Gold possesses the property of welding cold. Thus, thin leaves, foil, and other forms of gold are more especially adapted to the use of the dentist as a filling material. The small particles are welded together in one perfectly homogeneous mass as the filling is inserted. The finely divided metal, such as that thrown down in the preparation of pure gold from the chloride

solution, may be compressed between dies in the form of disks or medals.

The pure metal fuses at 1060 C. and its alloys at much lower temperatures. When heated much above its melting point it slowly volatilizes and is readily dissipated in vapor by the oxyhydrogen flame.

Pure gold is nearly as soft as lead, in consequence of which articles of jewelry, coin, etc., made from it are alloyed with copper, silver, platinum, etc., to give them the requisite hardness, durability, and elasticity.

The specific gravity of gold cast in an ingot is 19.265; when stamped, 19.31; and that of the precipitated metal from 19.55 to 19.72.

Graham has shown that gold is capable of occluding 0.48 of its volume of hydrogen, and 0.2 of its volume of nitrogen.

**GOLD BEATING.**—After the gold is precipitated from the chloride solution, it is thoroughly washed, dried, and melted in a clean crucible at a temperature higher than necessary to simply fuse it, by which its malleability is said to be improved. It is then poured into ingot molds previously heated and oiled, and cast into ingots, each one inch wide, one-fourth of an inch thick, and from four to eight inches in length. These are removed from the mold, cleaned in dilute sulphuric acid, washed and annealed. The ingot is next laminated by being repeatedly passed through heavy steam rollers, and annealed after each lamination, until it is formed into a ribbon one inch wide, about the thickness of tissue paper, and its length depending upon the original weight of the ingot.

The ribbons are then cut into pieces an inch square,

their thickness depending upon the number of the foil, 2, 4, 6, 10, etc., it is designed to prepare from them; some allowance being made for subsequent trimming, and the necessity for leaving the sheet of correct weight. These little squares are again cleansed, taken up by wooden pliers and placed between the leaves of a "cutch" made from vellum or ground parchment which holds about two hundred pieces. The cutch is then enclosed in parchment bands and beaten on a granite or marble block, securely and firmly set, with a hammer weighing from seventeen to twenty pounds. The hammer is short-handled, and is wielded by the beater with one hand, while with the other hand he holds and rotates the packet of gold.

Every few moments the cutch is opened and the gold examined; then split in half and the position of the pieces reversed, so as to bring the middle ones to the outside and those on the outside to the middle of the packet. During the beating the packet is continually rotated and turned, to distribute the force of the blows equally throughout the packet; at intervals it is taken up and rolled between the hands to overcome any adhesion that may have taken place between the leaves of metal and interposed parchment.

Considerable skill is required to produce a good quality of foil, the physical properties of the metal being capable of alteration by the too great rapidity of the process.

When the gold is beaten into sheets about three or three and a half inches square, or about the size of the leaves of the cutch, which requires from fifteen to twenty minutes, they are removed from the cutch by means of the wooden pliers, and placed piece by piece

in a second packet of larger size made of the same material and called a "shoder." If, however, the pieces are too thick to produce the required number they are cut into four pieces, and the process repeated in the cutch. The shoder is then placed in the parchment bands, and the beating continued until the gold again equals the size of the skins, which requires about twice the length of time as before.

After the last beating the pieces are carefully laid out one at a time on a calf-skin cushion lined with soft flannel; the blemished, broken and torn ones are laid to one side, and the perfect ones are cut into uniformly square sheets so familiar to the dentist, by means of an instrument carrying four edges of malacca reed called a wagon. The gold does not adhere to this as it does to the metal. The sheets are then accurately weighed and are ready for annealing

The **annealing** is an important and delicate process, and may be accomplished in several ways: in the muffle of a furnace, on heated platinum, or on platinum-wire gauze with a spirit-lamp beneath it. Whatever may be the means by which it is accomplished, it must be properly done, i. e., the temperature must be sufficient to thoroughly heat and soften it uniformly in every part of the sheet, without melting and thickening the edges.

From the first to the last step the most important consideration is absolute purity and cleanliness.

Each book of gold foil contains 1/8 of an ounce, 2½ pennyweight, or 60 grains. Each full sheet is 4 inches square, and the number of the foil indicates the weight of each full sheet. Thus, a book of No. 2 would contain 30 sheets 4 inches square of 2 grains each; No.

10, 6 sheets of 10 grains each; No. 30, 2 sheets (4 inches square) of 30 grains each, and so on.

**Corrugated foil** is supposed to have been an outcome of the great Chicago fire. When the safes of one of the depots were opened, it was found that the paper had burned to a crisp, and the foil in the form of what is now known as corrugated foil. It was tried by some, and found many friends. In making the corrugated foil today a miniature Chicago fire is used to burn the paper. The gold is beaten as described before to No. 4 foil. It is then placed, sheet by sheet, between paper and enclosed in an iron box, with weights on the gold. The iron box is then placed on a slow fire and allowed to smolder, care being taken not to ignite the paper. After smoldering, the heat is gradually let on until the paper becomes carbonized. As the paper shrinks, the gold shrinks with it. The carbon is then blown off, sheet by sheet, and we have what is called corrugated or crystalline gold.

**Cylinders.**—These sheets are then rolled upon themselves in a cylindrical form of desired thickness, and cut into the size and style of cylinders required.

The numbering of pellets or cylinders is so variable with the different manufacturers that it really means little, if anything. Some number them as follows: No. ¼, one-fourth, of a sheet of No. 4 foil, rolled and cut into pellets of varying length; No. ½, one-half of a sheet of No. 4 foil, rolled and cut into pellets; No. 1, a whole sheet of No. 4, and so on. The length of the pellets is also variable, and is designated as style A, B, C, etc., by some manufacturers.*

*Hood and Reynolds.

Cylinders are, in accordance with the manner in which they are rolled, known as *loose* and *compact.*

The former can only be made by the manufacturers, and are composed of several sheets of No. 4 corrugated cohesive foil laid loosely upon one another and rolled lightly around a smooth needle-like piece of steel. The needle is then removed and the cylinders are cut by a peculiar sharp tool into assorted sizes or styles.

The compact variety may be made by the operator in a similar manner except that the ends of the cylinder will necessarily be more compact, on account of the manner in which it is cut.

There are other forms of gold used, such as *mat, block, rope, tape, ribbon,* etc.

**Rolled Gold.**—The heavier foil, as Nos. 20, 30, 60, 160, etc., is usually prepared by rolling, instead of beating. Flattening by rolling elongates the fiber, instead of increasing its surface in all directions, and it is thought produces a foil of greater density and toughness, and, when annealed, greater softness. Such foil is exceedingly cohesive and tenacious. It is also made in the noncohesive variety.

**Gold and Platinum Foils.**—These are prepared in a variety of ways by several manufacturers of dental foils. Some by electrodepositing a surface of pure gold upon platinum foil. As a rule such combinations produce a filling more able to stand the stress and abrasive force of mastication.

**Crystal Gold.**—This form of gold was first introduced by A. J. Watts, who prepared it by precipitating gold from a chloride solution by means of oxalic acid, treating the precipitate with nitric acid and neutralizing

the acid by washing with ammonia. The crystalline substance was then thoroughly dried in a muffle, when it was ready for use. The preparation fell into disuse on account of its unreliable quality, frequently being contaminated with nitric acid and other foreign substances. It is now prepared by electrolysis from the chloride solution. Plates of pure gold are suspended in the solution which replace the metal as fast as it is deposited upon the platinum cathode. When prepared properly it is an unobjectionable material, but certain precautions must be observed in its use, as its manipulation is very deceptive.

**ANNEALING GOLD.**—This process has a two-fold purpose: (1) To remove any deleterious substances which may have accumulated on the gold through exposure, and (2) to soften and more perfectly restore its cohesive quality.

After gold has been exposed for some time to the action of the air and extraneous influences, it loses to a great extent, the qualities it possessed when first prepared, i. e., it loses its softness, cohesiveness, etc., but is partially, if not wholly, restored to its original condition by annealing.

This is accomplished by a variety of methods. The main consideration, however, is the employment of a flame of as great purity as possible, free from the evolution of such substances as sulphur, chlorine, phosphorus, carbon, and their compounds. Ethyl alcohol ($C_2H_5OH$) is considered to be one of the most convenient and desirable liquid fuels.

The gas flame from a small Bunsen burner is one of almost perfect combustion; has become quite popular, and may be conveniently used where the gold is not

annealed by passing through the flame. The most desirable means, perhaps, is found in the pure platinum coils which are heated to incandescence by the electric current.

It has been observed that more even and uniform results may be attained by annealing the gold in small quantities on heated mica, or platinum, since the portion of the pellet or foil held by the carriers is only slightly heated when passed through the flame. Gold is best annealed after cutting, as the action of the shears in cutting annealed foil tends to give it a "wire" edge by slightly condensing it.

**PROPERTIES OF GOLD FOIL.**—These are various and variable with the products of different manufacturers. The most prominent and important for the consideration of the dentist is that known as *cohesiveness.*

Most metals which possess the analogous property called weldability are weldable in proportion to the length of time they will remain in a plastic condition under heat without melting, but pure gold is weldable cold. It is not to be inferred that gold is the only metal which is weldable cold; on the contrary, the clean, pure surfaces of many metals, such as lead and copper, are quite coherent, but much difficulty is encountered in obtaining and keeping them in the necessarily pure state.

Gold prepared by the manufacturers is unfortunately given a variety of names, such as cohesive, semicohesive, noncohesive, hard, soft, etc., all of which relate to its property of cohesiveness, and are perplexing and misleading to the older practitioners, not to say students. Gold is either *cohesive* or *noncohesive.*

**Cohesive Gold** is simply pure gold. The greater its purity, the more perfect its cohesiveness. It is annealed and soft when it leaves the makers, and sheets of it laid upon each other will cohere by mere contact. As stated previously, after it is exposed to air and to extraneous influences, handled and jostled about, it loses, from contact with impurities, some of its cohesiveness, and from pressure, some of its softness. These two properties are, however, partially or fully restored by proper annealing.

**Noncohesive Gold.**—Since pure gold is cohesive by virtue of its purity, it is obviously conversely true that *non*cohesive gold is as it is from *im*purity. The process of preparing noncohesive gold is a trade secret which every manufacturer possesses as part of his stock in trade. The natural cohesiveness of gold may be overcome by slightly alloying with iridium or iron, but it is probable this property is generally destroyed by some surface treatment the foil receives. Noncohesive foil can not be made cohesive by annealing, because the impurity can not be removed by that means.

**Semicohesive foil is noncohesive** before and **cohesive** after annealing. It is evident that the process of annealing purifies it, thereby restoring its natural property.

The terms *"hard"* and *"soft"* are used by the makers and many practitioners to designate the cohesive and noncohesive varieties, respectively. These terms are, however, erroneous, and should not be used.

"The feeling of softness," says Dr. Kirk, "exhibited by noncohesive foil under the instrument is due largely to the fact of its noncohesiveness, whereby the several

laminæ slip or slide one upon another, thus conveying a yielding or soft sensation to the tactile sense, and making it possible to condense large masses at a time, the pressure being conveyed continuously throughout the mass and the condensation or consolidation being uniform. A similar mass of cohesive foil, treated in the same manner and under like conditions, presents a greater resistance to the instrument, and conveys the idea of hardness, from the fact that as pressure is applied the successive laminæ unite or weld together from the surface downward into a homogeneous stratum of metal, which offers greater resistance and becomes more impenetrable by constant additions to its thickness, until the condensing instrument fails to make any further impression; but upon removing the mass of gold it will be found that that portion of it which occupied the bottom of the cavity is still in the form of foil and not homogeneously condensed."

**Purity.**—The physical properties of gold are more apt to be influenced by lack of purity than by any other factor. Impurity may be occasioned by several means: first, by admixture of other metals, especially those easily oxidized. Second, by surface contamination caused by handling or exposure to vaporous gases. Third, by the absorption or occlusion of gases.

The following assays were made for Dr. Kirk by Messrs. Dubois and Eckfeldt, assayers of the United States Mint, Philadelphia. The table exhibits in thousandths the relative fineness of some of the foils in general use.*

*American System of Dentistry, iii, p. 842.

Each assay was duplicated:

| | | |
|---|---|---|
| No. 1. | Abbey's Non Cohesive.....998.8 | 998.7 |
| No. 2. | Wolrab's, from C. A. Timme..999.2 | 999.3 |
| No. 3. | Quarter-Century, S. S. White Dental Mfg. Co.....999.1 | 999.1 |
| No. 4. | Rowan's Decimal Foil from Gideon Sibley .....999.9 | 999.8 |

**Discoloration.**—The unfortunate discoloration of some gold fillings is in all probability due to a slight admixture of iron obtained during the precipitation from the chloride solution when ferrous sulphate is used, or from the iron ingot mold, or from the surface of the plugger point during the insertion of the filling.

**COMPOUNDS OF GOLD WITH OXYGEN.**—Gold forms two oxides:

**Aurous Oxide,** or *Monoxide,* $Au_2O$, is prepared by adding a solution of caustic potassa to the monochloride. It is a green, unstable powder, being easily decomposed into metallic gold and auric oxide.

**Auric Oxide,** or *Trioxide,* $Au_2O_3$, is prepared by adding magnesia to auric chloride; when the sparingly soluble aurate of magnesium thus formed is well washed and digested with nitric acid, auric oxide is left as an insoluble, reddish-yellow powder. It is easily reduced by heat or mere exposure to light; soluble in nitric, hydrochloric, and hydrobromic, and insoluble in hydrofluoric acid. Its acid properties are marked: it dissolves freely in alkalies. When digested with ammonia, it yields—

**Fulminating Gold.**—This compound is usually prepared, however, by the addition of ammonia to trichloride of gold. It is a buff precipitate, and explodes

violently when gently heated. Its formula is probably—

$$Au_2O_34H_3N.H_2O.$$

**ACTION OF ACIDS ON GOLD.**—Gold is not tarnished or affected by air or water at any temperature, nor by **sulphuretted hydrogen.**

Neither is it soluble in **sulphuric, nitric** nor **hydrochloric acid.**

In **nitrohydrochloric acid,** however, it speedily dissolves, forming the trichloride of gold, $AuCl_3$.

It is also attacked by a vapor or solution of **chlorine;**

By **bromine,** dissolving in bromine-water to form auric bromide, $AuBr_3$; and

By **iodine,** dissolving when finely divided in hydriodic acid by aid of the air and potassium iodide, forming potassium auric iodide—

$$2Au + 6HI + 2KI + 3O = 2KIAuI_3 + 3H_2O.$$

**Potassium cyanide** solution dissolves precipitated gold with the aid of air, forming potassium aurocyanide—

$$2Au + 4KCN + O = 2KAu(CN)_2 + K_2O.$$

**Purple of Cassius.**—So named from its color and from the name of its discoverer. It is much employed for imparting a rich red or reddish purple to glass and porcelain, and is of especial interest in dentistry, because it is used by the manufacturers of artificial teeth to produce the gum tint of dental porcelain. It is a vitrifiable material composed of gold, tin and oxygen. The proportion, however, is thought to be variable. It is generally given the formula—

$$Au_2O.SnO_2,SnO.SnO_2.4H_2O.$$

It is prepared by a variety of methods. Pelletier's is as follows: 20 grains of gold are dissolved in 100 grains of aqua regia containing 20 parts nitric to 80 parts hydrochloric acid; the solution is evaporated to dryness over a water-bath; the residue dissolved in water; the filtered solution diluted with seven or eight deciliters of water and tin filings introduced into it. In a few minutes the solution becomes brown and turbid and deposits a purple precipitate, which merely requires to be washed and dried at a gentle heat. The purple thus prepared contains, in 100 parts, 32.746 parts of stannic acid, 14.618 of protoxide of tin, 44.772 of aurous oxide, and 7.864 of water. The precipitate obtained by the addition of stannous chloride to auric chloride is always brown. To obtain a fine purple precipitate the auric chloride should be treated with a mixture of stannous and stannic chlorides.

The purple is now produced by a dry method, by the manufacturers of gum enamel. It consists of digesting an alloy of gold, tin, and silver in nitric acid. The method was discovered by the late Professor Elias Wildman. The proportions are as follows:

| | |
|---|---|
| Pure silver | 240 grains |
| " gold | 24 " |
| " tin | 17.5 " |

In preparing the alloy it should be melted and granulated four times to insure intimate admixture of the metals. It is afterwards placed in a flask and digested by the aid of gentle heat in chemically pure nitric acid in the proportion of 2 parts acid to 1 of water. After

the silver has all been dissolved the precipitate is allowed to settle, the supernatant liquid poured off and the precipitate washed several times with warm distilled water. It is then again subjected to the action of dilute nitric acid, aided by heat and continual stirring to dissolve any of the remaining silver. When all action subsides, pour the contents of the flask on a filter paper and wash *all* the nitrate of silver out with pure water. The filtrate should be frequently tested with sodium chloride. When the latter reagent will no longer throw down the white precipitate of chloride of silver, the precipitated purple of Cassius on the filter paper is dried and is ready for use in the manufacture of gum frit.

Purple of Cassius is completely soluble in ammonia, upon ignition, however, it becomes insoluble. "That ignition," says Dr. Kirk, "does effect such decomposition is proved by the fact that the ignited powder can have all of its gold extracted by aqua regia, leaving pure stannic oxide, or the gold may be extracted from it by amalgamation with mercury, which is impossible before ignition."

**ALLOYS.**—Gold very readily unites with most of the metals, forming alloys of varied qualities. When in the pure state gold is too soft for any great use other than for filling teeth; consequently the greater quantity of gold is alloyed with some metal that will increase its hardness and durability, without greatly impairing its more valuable qualities. The metals usually employed for this purpose are silver, platinum and copper.

**Silver** and gold are easily mixed together, but do not seem to form definite compounds. Such alloys are more fusible, more ductile, harder, more sonorous and elastic than gold, and are generally of a greenish-white color. One-twentieth of silver is sufficient to modify the color of gold. The alloys of gold and silver are known to jewelers as *yellow, green* and *pale gold,* according to the content of silver.

**Copper** and gold unite much more readily than silver and gold; indeed it is reasonable to believe from their behavior that a chemical combination is formed with 76 per cent of gold and 24 per cent of copper. Alloys of copper and gold are much harder, tougher, and more easily fused; less malleable and ductile, and greatly changed in color, being of a decidedly reddish tint, depending upon the proportion of copper with which the gold is debased. An alloy of gold 76, and copper 24, as referred to heretofore, is distinctly crystalline and quite brittle; but a larger proportion of either gold or copper restores the malleability of the alloy.

**Standard Gold.**—The standard alloy of most nations is one of copper and gold. Some contain small quantities of silver, but this is due to imperfect parting of silver and gold, or it may be contained in the copper used for the alloy. The proportion of copper to gold varies slightly in different countries, and such proportions are stated in thousandths; thus, pure gold is one thousand (1000) fine. The table on page 339 gives the composition of standard gold, as fixed by the nations mentioned.

| Nation | Gold | Copper |
|---|---|---|
| United States<br>France<br>Germany<br>Belgium<br>Italy<br>Switzerland<br>Spain<br>Greece<br>China<br>Austrian *Crowns* | 900 (Carat 21.6—) | 100 |
| Great Britain | 916 | 84 |
| Ducats, Hungarian | 989 | 11 |
| Ducats, Austrian | 986 | 14 |
| Ducats, Dutch | 982 | 18 |

The first United States gold coins were ten-dollar pieces, coined in 1795; they weighed 270 grains each, and were of 916.666 (22-carat) fineness. Their weight was reduced in 1834 to 258 grains, with 899.225 (21.581-carat) fineness; and in 1837 the present standard of 900 (21.599-carat) fineness was established.

Alloys of gold with copper, or with silver, or with both, are much used in the manufacture of jewelry. When the gold contains copper only, it is termed *red* gold when silver only, *white* gold; if the gold contains both metals, the caratation is termed *mixed.* In many countries a legal standard of fineness is fixed for gold ornaments and jewelry. In England gold is stamped, or *Hall Marked,* 16, 18, and 22-carat; in France, 18, 20, and 22-carat; in Germany, 8, 14, and 18-carat, and, also, under the term *joujou* gold, a 6-carat gold used for electroplated jewelry. The purpose of the stamping is to protect the purchaser, who is enabled to know the carat of the gold he is buying.

The following alloys used by jewelers are also of much interest to the dentist:

## TABLE OF MIXED CARATATION—*Brannt*

| Carats | Parts | | |
|---|---|---|---|
| | Gold | Silver | Copper |
| 23 | 23 | ½ | ½ |
| 22 | 22 | 1 | 1 |
| 20 | 20 | 2 | 2 |
| 18 | 18 | 3 | 3 |
| 15 | 15 | 3 | 6 |
| 13 | 13 | 3 | 8 |
| 12 | 12 | 3½ | 8½ |
| 10 | 10 | 4 | 10 |
| 9 | 9 | 4½ | 10½ |
| 8 | 8 | 5½ | 10½ |
| 7 | 7 | 8 | 9 |

## COLORED GOLDS—*Brannt*

| Parts | | | | | Color |
|---|---|---|---|---|---|
| Gold | Silver | Copper | Steel | Cadmium | |
| 2 to 6 | 1.0 | .... | .... | .... | Green |
| 75.0 | 16.6 | .... | .... | 8.4 | " |
| 74.6 | 11.4 | 9.7 | .... | 4.3 | " |
| 75.0 | 12.5 | .... | .... | 12.5 | " |
| 1.0 | 2.0 | .... | .... | .... | Pale yellow |
| 4.0 | 3.0 | 1.0 | .... | .... | Dark yellow |
| 14.7 | 7.0 | 6.0 | .... | .... | " " |
| 3.0 | 1.0 | 1.0 | .... | .... | Pale red |
| 10.0 | 1.0 | 4.0 | .... | .... | " " |
| 1.0 | .... | 1.0 | .... | .... | Dark red |
| 30.0 | 3.0 | .... | 2.0 | .... | Gray |
| 1 to 3 | .... | .... | 1.0 | .... | Blue |

## HIGHER CARAT COLORED GOLDS

| Parts | | | Color | Carat |
|---|---|---|---|---|
| Gold | Silver | Copper | | |
| 15 dwt. ..... | 2 dwt. 18 grs. | 2 dwt. 6 grs. | Yellow Tint..... | 18 K |
| 15 " ..... | 1 " 18 " | 3 " 6 " | Red " ..... | 18 K |
| 1 oz. 16 dwt. | 6 " ..... | 12 " ..... | Reddish Spring gold | 16 K |
| 1 oz..... | 7 " ..... | 5 " ..... | Yellow tint..... | 16 K |
| 1 oz..... | 2 " ..... | 8 " ..... | Red tint..... | 16 K |

Jewelers usually make their solders from the gold upon which they are to be used by the addition of small quantities of copper, silver or brass, the latter greatly increasing the fusibility and fluidity. The following are:

JEWELERS' SOLDERS

| For 18-Carat Gold. | | For 16-Carat Gold. | |
|---|---|---|---|
| 18-carat gold..... | 1 dwt. | 16-carat gold..... | 1 dwt. |
| Silver..... | 2 grs. | Silver..... | 10 grs. |
| Copper..... | 1 gr. | Copper..... | 8 grs. |

**Carat.**—The fineness of gold is also expressed in carats, a twenty-fourth part, formerly the twenty-fourth part in weight of a gold marc. It is now assumed that here are 24 carats in unity; whether the unit be one pound, one ounce, or one pennyweight, it is divisible into 24 equal parts, and each of these parts is called a carat to express fineness. If a quantity of gold is chemically pure, in other words contains no alloying elements, it is, as we have previously explained, 1000 fine; or, in other words, each 24th part is gold, and it is, therefore, said to be of 24-carat fineness. If, however, 2 carats, or $\frac{2}{24}$ths of the unit quantity are composed of one or more alloying metals, the gold is said to be 22 carats fine, or if 6 carats or $\frac{6}{24}$ths of the alloy is debasing metal, the carat is 18 fine, etc. The table on page 342 shows the equivalent of each carat in thousandths.

**GOLD PLATE.**—Pure gold is rarely employed in the dental laboratory, except for soldering continuous-gum cases and in some parts of crown and bridgework. Its extreme softness and flexibility make alloying absolutely necessary. The latter must be accomplished,

| Carats | Thousandths | Carats | Thousandths |
|---|---|---|---|
| 1 | 41.667 | 13 | 541.667 |
| 2 | 83.334 | 14 | 583.333 |
| 3 | 125.001 | 15 | 624.555 |
| 4 | 166.667 | 16 | 666.667 |
| 5 | 208.333 | 17 | 707.333 |
| 6 | 250.000 | 18 | 750.000 |
| 7 | 291.666 | 19 | 791.666 |
| 8 | 333.333 | 20 | 833.333 |
| 9 | 374.999 | 21 | 874.999 |
| 10 | 416.667 | 22 | 916.666 |
| 11 | 458.630 | 23 | 958.333 |
| 12 | 500.000 | 24 | 1000.000 |

however, without practically impairing either its malleability, or pliancy, and at the same time endow it with that degree of hardness, elasticity and strength necessary to resist the stress and wear to which an artificial denture is exposed in the mouth.

**Copper and Silver** are much used to debase or alloy, pure gold. It is questionable, however, whether copper should be used as almost universally as it is, indeed, some regard it as exceedingly objectionable. A plate made from a gold alloy containing a large percentage of copper is more easily tarnished, and has a disagreeable metallic taste, and may become a source of injury to the soft tissues of the mouth.

**Silver** exercises a very benign influence over copper contained in gold plate, controlling the tendency to that disagreeable redness. Equal parts of silver and copper have little or no effect upon the color of gold. Silver assists in imparting hardness, elasticity and durability to the alloy, without so far debasing it as copper alone.

**Platinum and silver** are sometimes used to endow pure gold with the qualities necessary for a dental

base; but the labor of swaging is very greatly increased when platinum is contained in the plate.

In order to secure the best results, alloys intended for plate should not be less than 18 carat fineness; and the alloy should contain as little copper as possible. It may even be unsafe to use a lower carat than 18.

The following are some of the formulas in use for the preparation of alloys for dental bases:

| Number of Formula | Carat | Parts Pure | | | |
|---|---|---|---|---|---|
| | | Gold | Silver | Copper | Platinum |
| * 1 | 18 | 18 dwts. | 2 dwts. | 4 dwts. | ..... |
| 2 | 18 | 18 " | 3 " | 3 " | ..... |
| 3 | 18 | 18 " | 4 " | 1 dwt. | 1 dwt. |
| * 4 | 19 | 19 " | 2 " | 3 dwts. | ..... |
| 5 | 19 | 19 " | 3 " | 1 dwt. | 1 dwt. |
| * 6 | 20 | 20 " | 2 " | 2 dwts. | ..... |
| * 7 | 21 | 21 " | 1 dwt. | 2 " | ..... |
| * 8 | 22 | 22 " | 18 grs. | 1 dwt. | 6 grs. |
| † 9 | 18 | 64½ dwts. ($60.00) | 13 dwts. | ..... | ..... |
| *10 | 18 | 20 dwts. | 2 dwts. | 2 dwts. | ..... |
| ‡11 | 18 | 516 grs. ($20.00) | 96.45 grs. 25c. coin | ..... | ..... |
| *12 | 19 | 20 dwts. | 40 + grs. | 25 grs. | ..... |
| *13 | 20 | 20 " | 20 + grs. | 18 grs. | ..... |
| ‡14 | 20 | 516 grs. ($20.00) | 10c. coin | ..... | ..... |
| *15 | 21 | 20 dwts. | 13 + grs. | ..... | ..... |
| *16 | 21 | 20 " | ..... | 6 grs. | 7½ grs. |

**CLASP GOLD.**—Gold for clasps, elastic wires, backings, stays, posts, dowels, etc., usually contains a small amount of platinum to give it greater strength and elasticity. The following formulas are recommended by Professor Chapin A. Harris:

| No. 1—20-Carat | | No. 2—20-Carat | |
|---|---|---|---|
| Pure gold | 20 dwts. | Coin gold | 20 dwts. |
| " copper | 2 " | Pure copper | 8 grs. |
| " silver | 1 dwt. | " silver | 10 " |
| " platinum | 1 " | " platinum | 20 " |

*Richardson's Mechanical Dentistry, p. 56.
†Johnson Bros.
‡Prof. C. L. Goddard.

A content of platinum in gold renders the alloy more liable to oxidation, and, says Professor Harris, "This effect is so marked that such an alloy is readily acted upon by nitric acid." It is not probable, however, that the small amount contained in clasp gold would affect its integrity.

**CROWN GOLD.**—Gold for crowns should combine strength with good color. Those alloys of a large copper content make exceedingly unsightly crowns, on account of their deep red color. Professor C. L. Goddard recommends the following for alloys the color of pure gold:

| No. 1—21.6-Carat | | No. 2—21.6-Carat | |
|---|---|---|---|
| Pure gold | 90 parts | Coin gold | 50 parts |
| " silver | 5 " | Pure gold | 45 " |
| " copper | 5 " | " silver | 5 " |

**GOLD SOLDERS.**—These are usually alloys of gold, silver, copper and zinc, and are designed to be a trifle more fusible than the parts to be soldered; this property is conferred upon them principally by the content of zinc (or brass). They should also possess considerable strength; too much base metal, therefore, should not be added, as it will, by oxidizing, tend to very materially weaken the alloys. Their carat should be as high or nearly as high as that of the plate, and color as nearly as possible the same.

The formulas on page 345 have yielded satisfactory results as gold solders.

A simple method for making a good solder suitable for the plate upon which it is to be used is: 5 parts of the plate and one of brass or of silver solder. In the

| No. | Carat | Parts | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | U.S. Coin Gold | Pure Gold | Pure Silver | Pure Copper | Pure Zinc | Brass | Spelter Solder |
| 1 | 14 | $10.00 | ..... | 4 dwts. | 2 dwts. | | | |
| 2 | 14 | 16 dwts. | ..... | 5 " | 3 dwts. 18 grs. | | | |
| 3 | 15 | 6 " | ..... | 30 grs. | 20 grs. | ..... | 10 grs. | |
| 4 | 16 | ..... | 11 dwts. | 3 dwts. 6 grs. | 2 dwts. 6 grs. | | | |
| 5 | 16+ | ..... | 11 dwts. 12 grs. | 3 dwts. | 1 dwt. 12 grs. | 12 grs. | | |
| 6 | 18 | 30 parts | ..... | 4 parts | 1 part | ..... | 1 part | |
| 7 | 18 | ..... | 27 parts | 4 " | 4 parts | ..... | 1 " | |
| 8 | 20 | $10.00 | ..... | ..... | ..... | ..... | ..... | 20.64 grs. |
| 9 | 20 | ..... | —5 dwts. | 12 grs. | 6 grs. | ..... | ..... | 6 grs. |
| 10 | 14 | (18 K. gold plate formula No. 9) 20 dwts. Johnson Bros. | | 2.5 dwts. | 20 grs. | 35 grs. | | |

case of coin gold, or the crown alloy given on page 343, a solder thus made will be exactly 18 carat.*

Zinc is best added to the alloys in the form of brass. The latter should be of a known formula, so that the desired amount of zinc may be accurately calculated; it should also be malleable and ductile; or the solder is apt to be very brittle.

*Prof. C. L. Goddard.

## RULES FOR COMPUTING AND COMPOUNDING GOLD ALLOYS† AND EXAMPLES‡

### PART I

To ascertain the carat of any given alloy, the proportion may be expressed as follows:

As the weight of the alloyed mass is to the weight of gold it contains, so is 24 to the standard sought.

EXAMPLE—Gold 6 parts, silver 2 parts, copper 1 part, total, 9 parts.

9:6::24:?

6

9)144

16 Answer.

Another method when alloyed gold is used in forming the mass, instead of pure gold, is to express the proportion as follows—

As the weight of the alloyed mass is to the weight of the gold alloy used in its composition, so is the carat of the latter, to the carat of the former.

EXAMPLE—Harris No. 1 solder:

| | | |
|---|---|---|
| 22-carat Gold | 48 | parts |
| Copper | 16 | " |
| Silver | 12 | " |
| Total | 76 | " |

76:48::22: x carat. Ans. 13.9 carat.

†Rules by Prof. Geo. Watt.
‡Examples by Prof. C. L. Goddard.

EXAMPLES UNDER RULE 1

1. Find the carat of 36 pennyweights of gold, 8 pennyweights of copper, 4 pennyweights of silver. Ans. 18 carat.

2. Find the carat of 9 pennyweights of gold, 2 pennyweights of copper, 1 pennyweight of silver. Ans. 18 carat.

3. Find the carat of 38 pennyweights of gold, 6 pennyweights of copper, 4 pennyweights of silver. Ans. 19 carat.

4. Find the carat of 22 pennyweights of gold, 1 pennyweight of copper, 18 grains of silver, 6 grains of platinum. Ans. 22 carat.

5. Find the carat of 22 pennyweights of gold, 2 pennyweights of copper, 1 pennyweight of silver, 1 pennyweight of platinum.

6. Find the carat of 6 pennyweights of gold, 2 pennyweights of copper, 1 pennyweight of silver.

7. Find the carat of 48 parts of 22-carat gold, 16 parts of silver, 12 parts of copper. Ans. 13.9 carat.

8. Find the carat of 20 pennyweights of gold coin, 2 pennyweights of copper, 2 pennyweights of silver. Ans. 18 carat.

9. Find the carat of 20 pennyweights of gold coin, 25 grains of copper, 40 + grains of silver.

10. Find the carat of 20 pennyweights of gold coin, 18 grains of copper, 20 + grains of silver.

11. Find the carat of 464.4 grains of gold, 5.16 grains of silver, 46.44 grains of copper.

## PART II

To reduce pure gold to any required carat, the proportion may be expressed as follows:

As the required carat is to 24, so is the weight of gold used to the weight of the alloyed mass when reduced. The weight of gold subtracted from this gives the quantity of alloy to be added.

Example.—Reduce 6 ounces of pure gold to 16 carat, 16:24::6 ounces: 9 ounces. 9—6=3 ounces alloy to be added.

To reduce gold from a higher carat to a lower carat, the proportion may be expressed as follows:

As the required carat is to the carat used so is the weight of the mass used to the weight of the alloyed mass when reduced.

The weight of the mass used, subtracted from this, gives the quantity of alloy to be added.

Example.—Reduce 4 ounces of 20-carat gold to 16 carat.

16:20::4 ounces: ?

$$\begin{array}{r} 4 \\ \hline 16)80 \\ \hline 5 \text{ ounces.} \end{array}$$

5 ounces — 4 ounces = 1 ounce alloy to be added.

### EXAMPLES UNDER RULE 2

1. Reduce 6 ounces gold to 16 carat. Ans. Add 3 ounces alloy.
2. Reduce 25 pennyweights gold to 18 carat. Ans. Add 8 pennyweights, 8 grains alloy.
3. Reduce 4 ounces of 20-carat gold to 16 carat. Ans. Add 1 ounce alloy.
4. Reduce 6 ounces of 18-carat gold to 15 carat.
5. Reduce 15 pennyweights of gold coin to 20 carat. Ans. Add 1.2 pennyweights.
6. Reduce 12 pennyweights of gold coin to 18 carat.
7. Reduce 4 pennyweights of 22-carat gold to 20 carat. Ans. Add 9.6 grains alloy.
8. Reduce 48 grains 20-carat gold to 16 carat.
9. Reduce 2 pennyweights 20-carat gold to 18 carat.
10. Reduce 1 pennyweight, 8 grains 18-carat gold to 16 carat.

## PART III

### To change gold from a lower to a higher carat, add pure gold or a finer alloy.

As the alloy in the required carat is to the alloy in the given carat, so is the weight of the alloyed gold used to the weight of the changed alloy required.

The weight of the *alloyed gold used* subtracted from this gives the amount of pure gold to be added.

Example.—Change 1 pennyweight of 16-carat gold to 18 carat. First subtract 16 and 18 from 24 to find the amount of alloy in each carat.

```
24    24
18    16
--    --
 6  : 8 :: 1 pennyweight : ?
      1
--    --
   6) 8
   ----
   1⅓ pennyweight.
```

1⅓ — 1 = ⅓ pennyweight of pure gold to be added.

## To change gold from a lower carat to a higher carat, by adding gold of a still higher carat.

Subtract the lower carat and the required carat each from the highest carat (instead of from 24) and proceed as before.

Example.—Change 2 pennyweights of 16-carat gold to 18 carat by adding 22-carat gold.

First subtract 16 and 18 from 22.

```
22    22
18    16
--    --
 4  :  6 :: 2 pennyweights : 3 pennyweights.
```

3 — 2 = 1 pennyweight of 22-carat gold to be added.

### EXAMPLES UNDER RULE 3

1. Change 1 pennyweight of 16-carat gold to 18 carat. Ans. Add 8 grains of gold.

2. Change 2 ounces of 16-carat gold to 20 carat. Ans. Add 2 ounces of gold.

3. Change 11 pennyweights, 8 grains of 18-carat gold to 20 carat.

4. Change 9 pennyweights of 16-carat gold to 18 carat. Ans. Add 3 pennyweights of gold.

5. Change 2 ounces of 20-carat gold to 22 carat.

6. Change 18 pennyweights of 16-carat gold to 18 carat by adding 22-carat gold. Ans. Add 9 pennyweights of 22-carat gold.

7. Change 3 pennyweights of 18-carat gold to 20 carat by adding gold coin. Ans. Add 3 pennyweights, 18 grains.

8. Change 12 pennyweights, 10 grains of 16-carat gold to 20 carat by adding gold coin.

9. Change 20 grains of 16-carat gold to 18 carat by adding 20-carat gold.

## MISCELLANEOUS EXAMPLES

1. Find the carat of 19 pennyweights of gold, 3 pennyweights of copper, 2 pennyweights of silver. Ans. 19 carat.

2. Reduce 5 pennyweights, 4 grains of gold to 20 carat.

3. Reduce 2 ounces, 4 pennyweights, 8 grains of 20-carat gold to 18 carat.

4. Reduce 12 pennyweights of 18-carat gold to 20 carat. Ans. Add 6 pennyweights of gold.

5. Find the carat of 20 parts of gold coin, 3 parts of copper, 3 parts of silver (gold plate).

6. Find the carat of 30 parts of gold coin, 1 part copper, 4 parts of silver, 1 part of brass (solder).

7. Reduce 258 grains of gold coin to 20-carat gold.

8. Reduce 516 grains of gold coin to 18-carat gold.

9. Reduce 4 pennyweights of 16-carat gold to 18 carat by adding gold coin.

10. Reduce 3 pennyweights, 6 grains of 16-carat gold to 18 carat by adding 20-carat gold.

($10 gold coin weighs 258 grains—$0.10 silver coin 38.58 grains.)

11. Add 10 cents silver to $20 gold—find weight and carat.

12. Add 25 cents silver to $20 gold—find weight and carat.

13. Change { Gold coin .....20 pennyweights; Copper ..... 2 "; Silver ..... 2 " } to formula for pure gold, and find carat.

14. Change { Gold coin .....20 pennyweights; Copper .....25 grains; Silver .....40+ " } do

15. Change { Gold coin .....20 pennyweights; Copper .....18 grains; Silver .....20+ " } do

16. Change { Gold .....18 pennyweights / Copper ..... 4 " / Silver ..... 2 " } to formula for gold coin, and find carat.

17. A watch chain, 14 carats fine, weighs 2 ounces, 4 pennyweights, 16 grains. How much pure gold must be added to raise it to 20-carat gold.

18. A piece of jewelry, 12 carats fine, weighs 3 pennyweights. How much U. S. gold coin must be added to make it 18-carat fine.

19. Add 4 ounces, 16 pennyweights, 5 grains of 14-carat gold to 2 ounces, 4 pennyweights, 16 grains of 16-carat gold and find the carat of the mixture. Ans. 7 ounces, 21 grains of 14.64-carat gold.

20. How much pure gold must be added to the above mixture to make it 18 carat fine.

21. How much U. S. silver coin and how much copper must be added to 3 ounces U. S. gold coin to reduce it to 18-carat gold containing equal parts of silver and copper.

---

The alloys of gold and most of the metals have been discussed under the heads of the various metals.

**TESTS FOR GOLD IN SOLUTION.—Sulphuretted Hydrogen** or **Ammonium Hydro-Sulphide** throws down a brown precipitate of auric sulphide ($Au_2S_3$). The second precipitant is not used, however, as the precipitate is soluble in it, as it also is in the alkaline sulphides. Auric sulphide is insoluble in nitric or hydrochloric acid taken, separately, but soluble in aqua regia.

**Ferrous Sulphate** and **Oxalic Acid** precipitate the gold in the metallic state; it is a brown powder, darker in the instance of the former than in the latter, but develops the color and luster of gold by being burnished with the finger-nail or instrument.

**Stannous** and **Stannic Chloride.**—The most delicate test for gold is probably the formation of the purple of Cassius.

**Heat and Light.**—Gold is reduced from many of its compounds by sunlight, and from all of them by more or less heat.

**Touchstone Tests.**—The touchstone used by assayers, gold bullion brokers and jewelers is a piece of smooth, fine grained black basalt. The metal to be tested is rubbed on the touchstone until it leaves a streak. Then various acids are added by a dropper and the effect noted. For instance, a supposed platinum alloy is rubbed on the stone, and dilute nitric acid is added. Platinum is insoluble in $HNO_3$: If silver, lead, or mercury be present, they will be converted into soluble nitrates. HCl. will precipitate white chloride of any of these metals. On adding ammonia, silver chloride if present will be redissolved. If it is lead chloride it will retain its white color and remain undissolved, and if it is mercury, the salt will turn black. Touchstone tests are merely test tube tests on a minute scale. Experts are capable of approximating the carat of a gold alloy by the color streak on a touchstone.

**ELECTRODEPOSITION OF GOLD.—By simple immersion.**—From an acid solution of gold chloride, the base metals, and silver, platinum, and palladium, deposit gold in the metallic state. In the **double cyanide of gold and potassium,** zinc will quickly become gilded, copper, brass, and German silver, slowly, and antimony, bismuth, tin, lead, iron, nickel, silver, gold, and platinum not at all.

**Deposition by a Separate Current.—The Solution.**—There are many solutions prepared for electrogilding, some being formed by chemical means, others by a separate current from the battery; but whether they are

made by chemical or electrical process, the best for a thick reguline deposit is the pure double cyanide of gold and potassium.

A cyanide solution may be prepared as follows:

Dissolve 120 grains of pure gold in one ounce of chemically pure aqua regia, and thus preparing the chloride of gold, as described previously.* Dissolve the chloride obtained in 32 ounces of warm distilled water, and add to it 1½ ounces of magnesia; the gold is precipitated. Filter and wash with pure distilled water, digest the precipitate in 10 parts of distilled water mixed with .75 part of nitric acid to remove magnesia; then wash the remaining oxide of gold with distilled water, until the wash-water exhibits no acid reaction with test-paper. Next dissolve 3 ounces of ferro-cyanide of potassium and 6 drams of caustic potash in 34 ounces of distilled water, add the oxide of gold prepared, and boil the solution about twenty minutes. When the gold is dissolved there remains a small amount of iron precipitated, which may be removed by filtering the solution. The liquid, a fine, clear, golden color, is then ready for use, to be employed either hot or cold, but a better and quicker deposit is nearly always obtained from the warm solution.

In **electroplating** objects the first essential is a finished surface, which must be made just as it is desired to be when completed. The next is cleanliness. If it be a silver denture or any other metallic object it should first be cleaned of all surface combinations, as oxides, sulphides, etc., by polishing in the ordinary way; then scrubbed with a solution of hot water and

*Preparation of Chemically Pure Gold, p. 319.

soap by means of a brass or steel scratch brush on the lathe; then washed or boiled in a strong solution of caustic potash, afterwards washing in distilled water, and finally in an acidulated water to remove all traces of the alkali.

The apparatus is exceedingly simple, consisting of a single battery cell and a glass bowl (preferably of perpendicular sides) to contain the solution. The latter may or may not be adjusted in a water-bath, according to whether the operator desires to work his solution hot or cold. Aside from these connecting and guiding wires cathode and anode hooks, together with an anode, a thermometer, a scratch brush, etc., are all that will be needed. The article to be plated is suspended by a hook in the solution from the cathode while a piece of pure gold is hung from the anode to keep up the strength of the solution, the latter electrode being easily determined by the fact that gas is liberated there by the passage of the current through the solution.

When a sufficient coating has been formed, the object is to be removed from the bath and burnished by the scratch brush or agate burnisher, moistened with a solution of warm water and soap, until the surface is finished as desired.

## CHAPTER XXI

## AMALGAMS

**An Amalgam is an alloy of two or more metals, one of which is mercury.**

The name is probably derived from the Greek *malagma* meaning a soft mass, and was applied to alloys of mercury on account of the increased plasticity and fusibility which it confers upon them.

Most metals, even hydrogen and the hypothetical metal, ammonium, unite directly with mercury to form a very interesting series of alloys which are termed amalgams. Many are extensively used in the arts and industries; but to no art or profession can they be of more interest or importance than to dentistry.

It must not be inferred that amalgams are to be given different chemical and physical theoretical consideration because they are studied thus distinctly. On the contrary, they are to be considered in every respect alloys, differing from the usual in no general way, except that *all contain mercury* and are endowed with some properties peculiar and dependent upon that metal. They are, therefore, subject to the same classification quoted from Matthiessen in the chapter on Alloys.* They offer an excellent opportunity for studying the behavior of metals towards each other, the examination being facilitated by the low temperature at which their combinations are effected.†

*The student should carefully review this classification.

†Mercury, it must be remembered, is simply a metal fused at ordinary temperatures.

The affinities affording the union of mercury with its constituents in the formation of amalgams are not as a rule, strong, for many of them are decomposable by pressure, and all by considerable heat; yet, like all other metals, mercury tends to form definite chemical compounds with certain metals. The following have been formed by combining the metals named with mercury and squeezing out the excess by means of hydraulic pressure to the amount of 60 tons to the square inch:

Amalgam of lead, $Pb_2Hg$.*
" " silver, $AgHg$.
" " iron, $FeHg$.
" " zinc, $Zn_2Hg$.
" " copper, $CuHg$.
" " platinum, $PtHg_2$.
" " gold, $Au_4Hg$.
" " tin, $Sn_2Hg$.

A native compound of mercury and silver, known as *Arguerite*, $Ag_6Hg$, is found crystallized in the form of the regular system.

Beautiful crystallizations of silver amalgam (*Arbor Dianæ*) may be formed in long prisms having the composition $Ag_2Hg_3$, by dissolving 400 grains of silver nitrate in 40 ounces of water, adding 160 minims of concentrated nitric acid, and 1840 grains of mercury; in a few hours beautiful crystals of considerable length will be deposited.

The union of mercury and other metals may be said to take place by four different means:

(1st.) *Some by direct contact,* accompanied in some

*Bloxam's Chemistry, Inorganic and Organic, p. 400.

instances by a considerable evolution of heat. Thus, if a piece of clean sodium be thrown upon a clean, dry surface of warmed mercury, union takes place with explosiveness, accompanied by incandescence, and the evolution of an amount of heat sufficient to volatilize portions of each metal.

(2d.) *Some by the action of mercury on a salt of the metal,* as the introduction of metallic mercury into a solution of a salt of the metal.

(3d.) *Others by the action of the metal on a salt of mercury,* as, the introduction of the metal into a solution of a salt of mercury.

(4th.) *By voltaic action* as when a metal is placed in contact with mercury in some acidulated solution.

**IN THE ARTS.—"Silvering."**—The process known as "silvering on glass" was until recently a misnomer, as tin amalgam was alone employed in the manufacture of mirrors.

The attraction of mercury for gold and silver is taken advantage of for the extraction of these metals from their ores. The addition of a little amalgam of sodium to mercury increases its combining power, and it more readily unites with other metals, even iron. This is especially recommended in the employment of mercury in the extraction of silver or gold from their ores.

An amalgam of equal parts of tin and zinc with six parts of mercury is much used for rubbers on electrical machines.

**DENTAL-AMALGAM ALLOYS.—The term comprehends those alloys composed principally of silver and tin, with the addition of small percentages of one or**

**more other metals (which, when comminuted and mixed with mercury, form a coherent mass).***

**A DENTAL AMALGAM may, therefore, be understood to be a comminuted** *metal* **or** *dental-amalgam alloy* **mixed with sufficient mercury to form a coherent mass.**

There are alloys which contain small percentages of mercury, added usually to lower their fusing points. Within the strict reading of the definition of amalgam these might be considered amalgams, but in the dental acceptation of the term they can not be regarded as such.

**HISTORY.**—The introduction of amalgam was not prompted by any specific merit that it had been demonstrated to possess, but was due solely to its properties of easy introduction, comparatively perfect sealing and prompt hardening, qualities which apparently recommend its wide and general use to those not possessing the requisite degree of skill for the successful manipulation of gold foil.

Applied upon a basis of glaring empiricism, with an absence of technical skill, the material received the prompt and sustained condemnation which its abuse had warranted. The steps and phases of this opposition of the trained and skilled against untrained and unskilled operators may be read in the dental journals of from 1846 to 1878, and even after. It was commonly known as the "Amalgam War."

The editor is greatly indebted to Dr. Wm. H. True-

*Such a distinction precludes the confusion of the terms "Dental Alloy" and "Dental Amalgam," the former of which we may understand as applicable to any of the numerous alloys used by dentists, for whatever purpose, and which do not contain, nor are designed to be mixed with, mercury; the latter being accepted as the Dental-Amalgam Alloy mixed with mercury.—Author.

man of Philadelphia for the following interesting bit of history of the early use of amalgams.

"M. Taveau did not introduce silver paste in 1826. He makes no mention of it in his various works until the 5th edition of his Hygiene de la Bouche, 1843. There he gives the process of making it, and says that he has been using it some six or eight years, and that it is the same that English dentists have been using under the name of 'Mineral Succeedaneum.' His work on cements for filling teeth, Paris, 1837, makes no mention of it.

"The advent of amalgam so far as known to me, is as follows: Joseph Fox, at the suggestion of Mr. Epps, a chemist of London, first used a fusible metal, the old Newton formula, for filling teeth in 1806, see advertisement in the second part of his work on the teeth. I have bound up with a copy of his work he presented to Mr. Epps, the identical letter there referred to, in which he asks the loan of an instrument devised by Mr. Epps for using the metal so that he could demonstrate its use to his class of dental students.

"Next Regnart (See Crowley's Dental Bibliography No. 897), in 1818, added mercury to lower the fusing point, and the amalgamated or fusible metal plus mercury was extensively used and continued to be used until about 1840 or perhaps later. J. L. Murphy (Crowley No. 1594), in 1837, published his method of preparing 'silver paste,' stating that he had used it with satisfaction for several years. He does not claim to be the inventor. He says it is not ideal, but serves a useful purpose for filling teeth so weak that gold can

not be used, and is a 'good thing to use until a better is found.'

"This writer also made and inserted porcelain inlays and gives his procedure, not, however, the first, for Mouton made gold shell crowns in 1746 and enameled those intended for the front teeth to match the adjoining teeth. In England, alloys of tin, silver, zinc, platinum, and gold, were used, amalgamated, for filling teeth early in the forties, and it was from England that Dr. Wm. M. Hunter obtained the formula, Tin 5, Silver 4, from which the amalgam fillings were made, which he showed to Dr. Townsend about 1853, and to others whom he invited to his office, during a meeting of the American Association of Dental Surgeons, then in session in Cincinnati. Townsend did not invent that formula, he never claimed to, but said Dr. Hunter gave it to him. Why it has been dubbed Townsend's alloy is a puzzle. It was not done until after his death.

"The History of the Amalgam War has not yet been written; when it is, we will speak more kindly of the Crawcours. They introduced into this country a filling material that is now indispensable to tooth-saving dentistry, and taught the dentists of this country to save teeth which they were ruthlessly extracting.

"Cadmium amalgam in a very short time destroyed tooth tissue, turning good solid dentine into a substance, the color and consistency of cheese rind for quite a distance around the filling."—April 26, 1912.

Soon after this time the "New-Departure Corps" was organized and espoused the cause of amalgams, and Dr. J. Foster Flagg made marked improvements in the

silver-tin alloy. To his conscientious and faithful adherence to the use of plastics is due much of the credit for the present status of dental amalgams.

The later investigations of Dr. G. V. Black have placed the study of amalgams upon a thoroughly scientific basis, and much may be expected from the work he so scientifically began.

**FORMATION OF DENTAL-AMALGAM ALLOYS.**— The directions for the preparation of alloys in general are equally applicable to the preparation of these special ones. The same precautions should be observed to avoid loss by oxidation, volatilization, etc. The manner of melting and pouring differs in no essential.

It will, therefore, suffice to briefly illustrate the process by detailing the manner of preparing one from the metals usually employed, such as tin, silver, and gold or copper.

The source of heat may be an open-grate, coke or coal fire, the forge, or what is best adapted to the purpose, the small injector gas furnace devised by Mr. Fletcher for melting metals. The crucible may be the ordinary refractory sand or Hessian, a clay and plumbago, or the plumbago crucible alone, the latter being preferable after it has been tested by heat. The crucible selected should be placed in the furnace and heated to a bright red heat; then a sufficient quantity of borax should be added to properly cover the inner sides when the crucible is tipped and rotated with the tongs.

The silver and gold or copper may now be added, preferably in small pieces of thinly rolled plate, and thoroughly heated until fused. Being sure that the

borax is melted as thin as possible, the tin may be added in as large pieces as convenient, that they may readily sink and unite with the fused metals before oxidation can take place. The crucible should then be removed with tongs, the contents well shaken or stirred with a stick of soft wood, and quickly poured into the previously warmed and oiled ingot molds, after which it is ready for comminution.

Borax is used as the flux, because it more perfectly protects the metals from oxidation and volatilization, absorbing the oxides that may have been previously formed or developed during the fusing; protects the molten metals from the rough and porous sides of the crucible, and facilitates the pouring.

The difficulty in adding tin is to avoid volatilizing any portion of it. It has been, therefore, melted separately, and the molten silver and gold or copper poured into it. This plan very thoroughly protects the tin, but it is questionable if the less fusible metals are not so chilled that their proper alloying is prevented. In such a case the ingot should be broken up and remelted under plenty of borax. An exceedingly good plan to avoid volatilization is to wrap the volatile metal in soft paper that will conform readily to the sides of the piece of metal and quickly dash it beneath the surface of molten borax. The paper quickly chars and serves both as a covering and reducing material.

The addition of zinc is probably the most difficult to accomplish without loss, as it so easily oxidizes. It is, therefore, sometimes united with a small amount of gold previously by wrapping the small grains of zinc in gold foil and thrusting them beneath the molten borax.

Bismuth, antimony, and the other more fusible metals, are alloyed with the mass similarly to tin. Platinum, palladium, and such, with the silver, or silver and gold melted as recounted above. The table of Dr. J. O. Keller (see pp. 364 and 365) gives the composition of some of the principal dental-amalgam alloys in use.

**Liquation,** or the separation of the constituents of the alloy, while molten or when being poured, on account of their differences in specific gravity and lack of affinity, may be best prevented by raising the alloy to a very high heat, stirring it with a stick of green wood, and pouring quickly. If it be suspected after pouring, the alloy should be remelted and again poured. Remelting is very apt to change the composition, and should be avoided where possible.

**COMMINUTION.**—Alloys are generally comminuted or broken up into small particles by rasping or filing into grains, or turned into shavings on the lathe.

An alloy rich in tin should be cut with a very coarse file, or, better, turned on the lathe, as it is frequently so soft that, clogging the file, it hinders further cutting. One rich in silver, however, presents a harder quality, and may be best comminuted with an ordinary coarse file.

After the alloy has been comminuted it should be passed through a fine wire sieve to remove all coarse pieces, borax, bits of wood, leather from the wire file-brush, and other undesirable admixtures. After this the filings should have a magnet passed through them until no iron filings adhere to it; they should then be spread out over a broad surface and carefully and gently blown, either by the breath or small bellows, to remove any dust.

## COMPOSITION OF SOME OF THE WELL-KNOWN DENTAL-AMALGAM ALLOYS

| | Tin | Silver | Gold | Platinum | Copper | Zinc | Cadmium | Antimony | Palladium |
|---|---|---|---|---|---|---|---|---|---|
| Arrington's (S. S. White's) | 57.5 | 42.5 | | | | | | | |
| Blackwood's Gold and Platinum Alloy | 56.85 | 42. | .5 | .15 | ..... | .5 | | | |
| Best (Spencer & Crocker's) Old | 61.5 | 34.5 | ..... | .5 | 3.5 | | | | |
| Chicago Refining Co's (Old) | 56. | 37. | 5. | 2. | | | | | |
| " " (New) | 58.37 | 37.55 | 4. | .1 | | | | | |
| Chase's Coppered Amalgam | 50. | 50. | ..... | ..... | 10. | ..... | ..... | .5 | |
| " Plastic Tin Amalgam | 50. | 50. | ..... | ..... | ..... | ..... | ..... | 7. | |
| " Alcohol Tight Amalgam | 40. | 50. | ..... | ..... | ..... | ..... | ..... | 10. | |
| " Stannous Gold | 40. | 40. | 20. | | | | | | |
| " Incisor Tooth Amalgam | 40. | 50. | ..... | ..... | ..... | ..... | ..... | 10. | |
| Caulk's White Alloy | 55. | 43.65 | ..... | ..... | 1.35 | | | | |
| " Par-Excellence | 61.75 | 27.25 | .15 | .25 | 10.6 | | | | |
| Crown Gold Alloy | 52.85 | 47. | .15. | | | | | | |
| Dawson's White Alloy | 49.27 | 48.24 | .05 | ..... | ..... | 2.41 | ..... | ..... | Trace |
| " Superior Amalgam | 63.55 | 31.85 | .65 | .15 | 2.35 | 1.45 | | | |
| Dibble's White Amalgam | 49.65 | 49.75 | .2 | ..... | ..... | .4 | | | |
| Fry's Amalgam | 53.8 | 44.35 | ..... | .9 | ..... | 1.05 | | | |
| Fletcher's Gold Alloy (Old) | 56. | 40. | 4. | | | | | | |
| " Platinum and Gold Alloy | 50.35 | 43.35 | 3.35 | 1.3 | 1.65 | | | | |
| Flagg's Submarine | 35. | 60. | ..... | ..... | 5. | | | | |
| " Facing | 35. | 37. | 5. | ..... | ..... | .3 | | | |
| " Contour Alloy | 37. | 58. | 5. | | | | | | |
| Globe (S. S. White's) | 53.36 | 44.74 | 1.5 | 4. | | | | | |
| Grime's Front Tooth (Old) | 44. | 10. | ..... | ..... | ..... | ..... | 46. | | |
| Hood's Amalgam (Old) | 60.25 | 37. | 2.75 | | | | | | |
| Hood & Reynold's Gold and Platinum Alloy | 50.4 | 44.3 | 3.8 | .3 | ..... | 1.2 | | | |
| High Grade Alloy (7½ per cent Gold) | 41.5 | 49. | 7.5 | ..... | ..... | 2. | | | |
| Harris' (Prof. J. H.) Amalgam | 48.1 | 40. | ..... | ..... | 4.9 | 7. | | | |
| Johnson & Lund's Extra (Old) | 60. | 38. | 1.5 | .5 | | | | | |
| " " " (New) | 61.15 | 36.75 | .15 | .5 | ..... | ..... | 1.45 | | |
| " " Virgin White Alloy | 61.65 | 37.75 | ..... | ..... | ..... | .6 | | | |
| " " Atlas Amalgam | 61.9 | 36.85 | ..... | .35 | ..... | ..... | .9 | | |
| " " Extra Tough Alloy | 51.25 | 47. | .3 | .2 | .25 | | | | |
| Justi's Superior Gold and Platinum Alloy | 59.1 | 35.2 | .32 | .08 | 3.5 | 1.8 | | | |
| King's Occidental | 54.75 | 42.75 | ..... | ..... | ..... | 2.5 | | | |

COMPOSITION OF SOME OF THE WELL-KNOWN DENTAL-AMALGAM ALLOYS—Continued

| | Tin | Silver | Gold | Platinum | Copper | Zinc | Cadmium | Antimony | Palladium |
|---|---|---|---|---|---|---|---|---|---|
| Lawrence's (Old) | 47. | 47. | 1. | ..... | 5. | | | | |
| " (New) | 50.43 | 44.06 | ..... | ..... | 5.51 | | | | |
| Moffitt's (Old) | 62. | 36. | 2. | | | | | | |
| The Dentist's Amalgam | 59.5 | 37.9 | ..... | ..... | ..... | 2.6 | | | |
| Oliver's Amalgam (Old) | 50.8 | 46.1 | 1.7 | 1.4 | | | | | |
| " White Amalgam (New) | 55.25 | 44.74 | | | | | | | |
| Peirce's (Old) | 40. | 55. | 4. | ..... | ..... | 1. | | | |
| Prof. Essig's (Old) | 55. | 45. | 2.5 | 2.5 | | | | | |
| Parson's Eureka Silver Alloy | 40. | 55. | ..... | ..... | 3. | 2. | | | |
| Sterling Amalgam (Old) | 62. | 31. | 1. | ..... | 6. | | | | |
| " " D. & L. (New) | 62.37 | 33.2 | ..... | .14 | 4.33 | | | | |
| Standard Amalgam (Davis & Co.) | 55.4 | 44.6 | | | | | | | |
| " Dental Alloy (Eckfeldt) | 40.6 | 52. | 4.4 | ..... | 3. | | | | |
| Shattuck's Standard Gold Alloy | 51.74 | 46.98 | 1.2 | .08 | | | | | |
| Sibley's Gold and Platinum Alloy | 54.65 | 43.15 | .2 | 2. | | | | | |
| Temporary Alloy | 88. | 10. | ..... | ..... | ..... | 2. | | | |
| Townsend's (Old) | 58. | 42. | | | | | | | |
| " (Improved) | 54.5 | 44.5 | 1. | | | | | | |
| Walker's (Old) | 69. | 30.5 | ..... | .5 | | | | | |
| " Excelsior Gold and Platinum Alloy | 51.5 | 42. | .3 | .2 | 6. | | | | |
| Welch's Gold and Platinum Alloy (Old) | 54. | 44. | 1.3 | .7 | | | | | |
| " " " " " (New) | 51.9 | 40. | 1.7 | .4 | | | | | |
| " Amalgam | 51.52 | 48.48 | | | | | | | |
| *1. Twentieth Century | 27.13 | 67.03 | ..... | ..... | 4.87 | 1.10 | | | |
| *2. True Dentalloy | 27.13 | 65.91 | ..... | ..... | 5.21 | 1.52 | | | |
| *3. Standard Alloy | 35.03 | 53.55 | 8.82 | ..... | 2.76 | ..... | | | |
| *4. Fellowship Alloy | 26.80 | 67.45 | ..... | ..... | 5.73 | 0.55 | | | |
| *5. Odontographic Alloy | 26.48 | 66.87 | 0.28 | ..... | 6.21 | trace | | | |
| *6. C. Ash Sons Co. (C. A. S.) Alloy | 27.16 | 66.54 | ..... | ..... | 5.02 | 0.90 | | | |
| University of California Dental Amalgam Alloy (White) Hodgen | 53. | 42.3 | ..... | ..... | 4.7 | ..... | | | |
| Made from Mexican Dollar 47 parts, Tin 53 parts | | | | | | | | | |

*Analysis of these popular proprietary alloys was made for the New York Institute of Stomatology by Dr. P. S. Burns, of the Massachusetts Institute of Technology.

A finely cut alloy takes up more mercury, contracts more, and is more plastic than a coarsely cut one, according to Dr. Black, who also says: "The cut in medium coarse filings—not so coarse as to seriously interfere with making a reasonably smooth mass—makes a much stronger amalgam, and one that contracts less with a given percentage of silver below 60 per cent than if cut fine."

**AGEING.**—Freshly comminuted alloys have been found to undergo a change as regards their affinities and working properties after a time. Investigation tends to demonstrate that this change is more directly due to temperature than time. For example: a certain alloy may be freshly comminuted and an amalgam made of it immediately, which upon examination is found *not* to *shrink,* but on the contrary may *expand.* The fresh comminution may then be subjected to a slightly elevated temperature for a short time and an amalgam afterwards made of it which will be found to *shrink.*

Dr. Black suggests the following explanation for the change: "In the cutting of an alloy the violence used hardens it, producing an allotropic condition of the metal, in which its chemical relations to mercury are profoundly changed. High temperatures, or even ordinary temperatures acting for a considerable time, have the effect of annealing the cut alloy and restoring its normal condition."*

Freshly cut alloys may be artificially aged, according to Dr. Flagg, by placing the comminuted alloy in any convenient receptacle and subjecting it to the

*Physical Properties of Silver-Tin Amalgams, Dental Cosmos, xxxviii, p. 976.

temperature of a boiling water bath for ten or fifteen minutes. Dr. Black considers "low temperature ageing" superior. "The ageings at 43° C. and the ageings in the sun [at 35° to 40° C.] produce the best working property." The author has found that these low temperature ageings require several days in the sun or forty-eight to sixty hours when the heat is continuous at 43° C.

The student naturally inquires: Should all alloys be

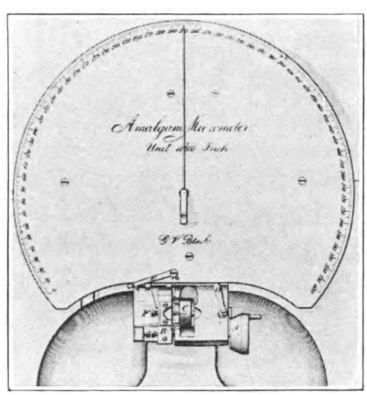


Fig. 59.—Dr. G. V. Black's amalgam micrometer.

aged before using; or how shall we determine which should and which should not? Dr. J. Foster Flagg claims that "there is no alloy made that does not work better results after it has been cut several weeks;" that those used freshly cut "shrink notably, set slowly, bulge markedly, and have little or no edge-strength."

By exceptionally painstaking experiments and accurate deductions from them, Dr. Black furnishes us

TABLE OF UNMODIFIED SILVER-TIN ALLOYS*

| Formulae | | How Prepared | Per Cent of Mercury | Shrinkage in Ten-Thousandths of an Inch | Expansion in Ten-Thousandths of an Inch | Percentage of Flow | Pounds Crushing Stress |
|---|---|---|---|---|---|---|---|
| Silver | Tin | | | | | | |
| **40** | **60** | **Fresh-Cut** | **45.78** | **6** | **7** | **40.15** | **178** |
| 40 | 60 | Annealed | 34.14 | 9 | 3 | 44.60 | 186 |
| **45** | **55** | **Fresh-Cut** | **49.52** | **4** | **8** | **25.46** | **188** |
| 45 | 55 | Annealed | 32.13 | 11 | 1 | 28.57 | 222 |
| **50** | **50** | **Fresh-Cut** | **51.18** | **2** | **2** | **22.16** | **232** |
| 50 | 50 | Annealed | 37.58 | 17 | 1 | 21.03 | 245 |
| **55** | **45** | **Fresh-Cut** | **51.62** | **2** | **2** | **19.66** | **245** |
| 55 | 45 | Annealed | 40.11 | 18 | 0 | 17.53 | 276 |
| **60** | **40** | **Fresh-Cut** | **52.00** | **1** | **0** | **9.06** | **239** |
| 60 | 40 | Annealed | 39.80 | 17 | 0 | 14.10 | 297 |
| **65** | **35** | **Fresh-Cut** | **52.00** | **0** | **1** | **3.67** | **290** |
| 65 | 35 | Annealed | 33.00 | 10 | 0 | 5.00 | 335 |
| **70** | **30** | **Fresh-Cut** | **55.00** | **0** | **14** | **3.45** | **316** |
| 70 | 30 | Annealed | 40.00 | 7 | 0 | 4.67 | 375 |
| **72.5** | **27.5** | **Fresh-Cut** | **55.00** | **0** | **42** | **3.92** | **275** |
| 72.5 | 27.5 | Annealed | 45.00 | 3 | 0 | 3.76 | 362 |
| **75** | **25** | **Fresh-Cut** | **55.00** | **0** | **60** | **5.64** | **258** |
| 75 | 25 | Annealed | 50.00 | 0 | 6 | 5.40 | 300 |

TABLE OF MODIFIED SILVER-TIN ALLOYS*

| Formulae | | | How Prepared | Per Cent of Mercury | Shrinkage in Ten-Thousandths of an Inch | Expansion in Ten-Thousandths of an Inch | Percentage of Flow | Pounds Crushing Stress |
|---|---|---|---|---|---|---|---|---|
| Modifying Metal | Silver | Tin | | | | | | |
| | **65** | **35** | **Fresh-Cut** | **52.33** | **0** | **1** | **3.67** | **290** |
| | 65 | 35 | Annealed | 33.00 | 10 | 0 | 5.00 | 335 |
| | **66.75** | **33.25** | **Fresh-Cut** | **51.52** | **0** | **4** | **3.35** | **329** |
| | 66.75 | 33.25 | Annealed | 33.53 | 7 | 0 | 5.06 | 380 |
| **Gold 5** | **61.75** | **33.25** | **Fresh-Cut** | **47.56** | **0** | **1** | **4.62** | **330** |
| Gold 5 | 61.75 | 33.25 | Annealed | 30.35 | 7 | 0 | 6.07 | 395 |
| **Platinum 5** | **61.75** | **33.25** | **Fresh-Cut** | **51.87** | **0** | **9** | **9.68** | **273** |
| Platinum 5 | 61.75 | 33.25 | Annealed | 37.33 | 7 | 0 | 8.20 | 352 |
| **Copper 5** | **61.75** | **33.25** | **Fresh-Cut** | **53.65** | **0** | **23** | **2.38** | **343** |
| Copper 5 | 61.75 | 33.25 | Annealed | 35.60 | 5 | 0 | 3.50 | 416 |
| **Zinc 5** | **61.75** | **33.25** | **Fresh-Cut** | **56.65** | **0** | **68** | **1.83** | **290** |
| Zinc 5 | 61.75 | 33.25 | Annealed | 40.65 | 0 | 9 | 2.07 | 345 |
| **Bismuth 5** | **61.75** | **33.25** | **Fresh-Cut** | **46.26** | **0** | **0** | **4.78** | **288** |
| Bismuth 5 | 61.75 | 33.25 | Annealed | 23.67 | 6 | 0 | 5.58 | 308 |
| **Cadmium 5** | **61.75** | **33.25** | **Fresh-Cut** | **57.57** | **0** | **100** | **6.40** | **225** |
| Cadmium 5 | 61.75 | 33.25 | Annealed | 47.25 | 0 | 5 | 3.54 | 290 |
| **Lead 5** | **61.75** | **33.25** | **Fresh-Cut** | **44.17** | **0** | **1** | **4.88** | **290** |
| Lead 5 | 61.75 | 33.25 | Annealed | 32.76 | 10 | 0 | 7.18 | 276 |
| **Aluminum 5** | **61.75** | **33.25** | **Fresh-Cut** | **65.00** | **0** | **445** | | |
| **Aluminum 1** | **64.5** | **34.5** | **Fresh-Cut** | **46.98** | **0** | **166** | **12.60** | **198** |
| Aluminum 1 | 64.5 | 34.5 | Annealed | 38.26 | 0 | 48 | 17.90 | 213 |

*See footnote on p. 369.

with a very scientific study of these changes as shown in the tables on silver-tin alloys above. Contrary to Dr. Flagg's views, he demonstrates that the

value of ageing depends upon the formula of the alloy. For example, an alloy of silver 65 and tin 35, made into an amalgam, when freshly cut *shrunk not at all; but,* instead, *expanded* .0001 inch. An amalgam made of the same alloy, after annealing *shrunk* .0010 inch. On the other hand, an alloy consisting of silver 72.5 and tin 27.5 freshly cut and made into an amalgam *expanded* .0042 inch, while the amalgam made of the same alloy annealed *shrunk* .0003 inch. As will be seen by the preceding tables of Dr. Black's, annealing seems to decrease the expansion and increase the shrinkage.

As a solution to the foregoing inquiry: If the operator prefers to use freshly cut alloy, the comminution should be followed immediately by amalgamation, and the amalgam thus made should be such as will neither shrink nor expand, or at least these changes should be as near zero as possible. On the other hand dealers and users of aged alloys must see to it that the alloy is of such a formula that age, either natural or artificial brings these changes of expansion and contraction of the amalgams made from them down to a minimum.*

**MERCURY.**—The percentage of mercury required for the amalgamation of these different alloys varies greatly. If too much be added in mixing, the resulting solution becomes so liquid that it is worked with difficulty, if at all; if too little, the mass of alloy lacks coherence and homogeneity, and the result of its attempted working is unsatisfactory. The mercury, of course, should be pure. Any admixture or chemical combination of a foreign substance necessarily serves to weaken the affinities of the mercury, resulting in

*The student should be directed to Dr. Black's article, Physical Properties of Silver-Tin Amalgams, Dental Cosmos, Vol. xxxviii, p. 965.

less mass strength of the compounds developed or metallic solution made.

There is no doubt amalgams are largely chemical compounds formed in definite chemical proportions with a mutual satisfaction of exacting affinities. The study of amalgamation; the solution formed when the alloy and mercury are brought into combination; the tendency to crystallization, accompanied by an evolution of more or less heat, and the peculiar, softly grating sound produced by compressing and rubbing the mix in the hand, sometimes called the "crepitus," re-

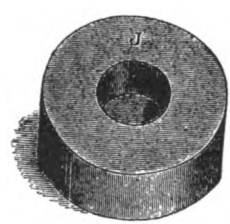


Fig. 60.—Wedelstædt test tube.*

sulting from the passing or sliding of the crystalline particles over each other, and other phenomena, admit of no other conclusion. We are, then, to bear in mind still the four conditions suggested by Matthiessen: "An alloy [*or amalgam*] may be either, (first) a solution of one metal in another; (second) a chemical combi-

*The Wedelstædt test tubes, in which these fillings were inserted for examining them under the microscope, and for other tests, are made of hardened steel one-half inch deep and one inch in diameter, with a cavity three-eighths of an inch in diameter, and one-fourth of an inch deep. The face or top of the tube is ground flat on a hone, and the margin or the cavity brought to a perfect edge. They are so arranged as to place them on the stage of the microscope, and rotate them so as to bring every part of the margin of the cavity under the lens in the same relation to the angle of the rays of light chosen for the examination.—*Black.*

In the illustration the test tube is empty.

nation; (third) a mechanical mixture; or, (fourth) a solution or mixture of two or all of the above.

The increase of the silver component above 60, and especially above 65, per cent, requires a very notable increase in the amount of mercury necessary. "With 70 per cent of silver," says Dr. Black, "it becomes very difficult to form a workable mass with 50 per cent of mercury, while with 80 per cent of silver it becomes necessary to use as much as 60 per cent of mercury. The disposition to expand becomes notable in connection with this increase in the amount of mercury required. An increase in the amount of mercury required is also noted in descending the scale of the percentage of silver in the range below 60 per cent, though this increase is less marked. It seems from careful observation on this point that a good working mass can be made with less mercury at about 60 per cent of silver than with any other proportion."

**Aged** alloys require a less percentage of mercury than the freshly cut of the same formula. An excess of uncombined mercury over a certain percentage weakens the mass.

**AMALGAMATION.**—The union of one or more metals or an alloy with mercury.

This is accomplished usually by adding the mercury in excess to the comminuted alloy in the palm of the hand, mixing and kneading it into a pliant mass, and wringing out the excess through muslin or chamois skin by means of heavy pliers.

Some prefer to add the mercury in excess to the comminuted alloy in a Wedgwood or ground-glass mortar directly, or, after mixing in the hand, then knead-

ing into a pliant mass in the mortar and squeezing out the excess of mercury as before.

Again, a great deal of pains is often taken to accurately determine the amount of mercury necessary for a given alloy or formula, and that determined amount is accurately weighed out and added for each separate mix.

A variety of instruments and apparatus has been introduced for weighing and mixing, but it is probable that most practitioners adhere to the method of mixing in the hand, as first described. It may be urged that such a method is empirical and unscientific, but such is not the case. On the other hand, it appears to the writer as most impracticable to endeavor to calculate the exact amount of mercury necessary to combine a comminuted alloy of given formula into a coherent mass. The influences which increase or diminish the required amount are too numerous and difficult to anticipate. For instance: The affinity of metals acting separately with mercury is one thing, while the affinity of the same metals combined and then united with mercury is entirely another. It is improbable that two melts of the same alloy will be exactly alike, and quite possible that two portions of the same ingot carry a different formula. The manner of comminuting is not always the same; a great difference in the amount necessary for finely and for coarsely comminuted alloy is observed; age of the alloy has a very marked effect, as does the manner of mixing and manipulation.

But if the mercury be added to the alloy in excess, and the affinity of the compound, mixture, or solution (as may be) be satisfied, demonstrating its satisfaction

by crystallization, and the excess filtered out, it seems to the writer just as scientific as the crystallization of any salt from its solution by the process of filtration and evaporation.

It is particularly important in the mixing and working of an amalgam that the mercury be evenly distributed throughout the mass, and that all violence, such as grinding in a mortar or squeezing in a vise, be avoided, as it tends to weaken the amalgam. Dr. Black says, "Grinding in a mortar causes an alloy to take up more mercury than when mixed in the hand or in a rubber mortar, but even when given the same percentage of mercury the product is weaker."

**EXPANSION AND CONTRACTION.**—The coefficient of expansion or contraction can not be demonstrated as constant for the same amalgam, for the fact that it is quite improbable that two ingots of an alloy can be made alike; that each mix will contain the same amount of mercury; or that all will be cut, mixed or manipulated the same.

Some amalgams both shrink and expand. The shrinkage occurring as the first and more rapid movement and expansion following slowly for several days. This dual movement is greatest in amalgams made from the silver 40 and tin 60 alloy,* diminishing with the increase of silver, and is seldom seen after passing a 60 per cent content of that metal. Ageing or annealing the cut alloy increases the shrinkage and decreases the expansion following it.

**Expansion.**—Silver seems to influence expansion greatly we find as we study Dr. Black's experiments. An alloy of silver 65 and tin 35, freshly cut, amalga-

*See table, p. 368.

mated and packed in a Wedelstædt test line,* expands .0001 of an inch after setting. This tendency to expand rapidly increases as the content of silver is increased; when at the point of silver 75, and tin 25, amalgams made of the freshly cut alloy expand .0060. Annealing brings the first (silver 65, tin 35), down to .0010 *contraction,* and the last (silver 75, tin 25), to only $\frac{1}{10}$ of the original expansion, viz., .0006 of an inch.

A content of 5 per cent platinum† seems to somewhat increase expansion, copper more so, zinc still more,

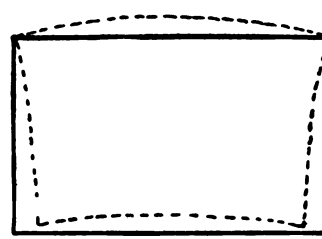


Fig. 61.

cadmium still greater, and aluminum very greatly. Aluminum 5, silver 61.75, tin 33.25, forms an alloy which when amalgamated, expands .0445. These expansions are all greatly reduced by annealing. The greatest expansion found in amalgams made from fresh-cut alloys used as filling material is in one composed of silver 75, tin 20, and copper 5, which expanded .0123. The appearance of an expanded amalgam is similar to that of ice at the mouth of an iron tube in which water has been frozen.

**Contraction.**—Tin has been said to influence a con-

*See p. 370 for description of this test tube

†See table of Modified Alloys, p. 368.

traction in amalgam. Considering Dr. Black's experiments on silver-tin amalgams we find the greatest contraction in amalgams made from the freshly-cut alloy is obtained from the silver 40, tin 60 alloy (.0006). This change represents its first movement, however, and is followed by an expansion of .0007, leaving the amalgam finally *expanded* .0001 of an inch. This is altered by annealing to a primary contraction of .0009, followed by an expansion of .0003, leaving a final contraction of .0006 of an inch. In contraction the mass tends to assume the form shown in Fig. 61.

The greatest shrinkage in an amalgam used as a filling material is found in that made from silver 54.86, tin 48.89, and zinc .25, which reached .0020 of an inch.

The greatest shrinkage in annealed alloys occurs from the alloy, silver 55 and tin 45, when the ultimate contraction is marked at .0018.

Strangely enough 5 per cent content of bismuth or lead increases the contraction when added to silver-tin alloys.

Copper amalgam is the only amalgam tested by Dr. Black which underwent no change of form in hardening or setting.

**SPHEROIDING OF AMALGAMS.**—It is reasonably held by most experimenters and writers that the composition, methods of mixing, and handling of some amalgams tend to promote an inherent disposition to assume a spheroidal or globular form on perfectly hardening. This, it is claimed, is manifested in the fillings made of these alloys, in that they raise out of and draw away from the sides of the cavity. No doubt much of this apparent elevation is, in reality, due to slovenly work, extending the filling material over the

margins of the cavity and building it fuller than necessary; subsequently a lack of edge-strength in the amalgam permits the portions so extended to be broken off, giving the plug the appearance of having been raised from its cavity.

Dr. Black ascribes it to the expansion and flow of the mass: it being confined, has a tendency to rise up in the center, assuming a spheroidal form, much as ice does when forming in a glass, due to the flow produced by the stress caused from the expansion of the ice against the unyielding sides of the vessel.

The cause of the spheroidal tendency has commonly been ascribed to the influence of tin; but of all the different amalgams tested by Dr. Black he found but two in the number which spheroided. Their formulæ are as follows, and were made from freshly cut alloy:

| 1. | 2. |
|---|---|
| Silver .....80 | Silver .....75 |
| Tin .....20 | Tin .....20 |
| Mercury.....60 *per cent* | Copper ..... 5 |
| | Mercury...56.56 *per cent* |

No. 1. "Margins much raised with spherical surface spheroided, 11.1."

No. 2. "Spheroided, 12.3."

From such results we might conclude that the spheroidal tendency is caused by the excess of silver or mercury, or both; but such a conclusion can not be safely drawn, nor is the problem one easy of solution, since it unquestionably involves the chemical affinities brought into play under these conditions.

**RESISTANCE TO STRESS.***—A silver-tin amalgam, when fully hardened, presents a hard, brittle, metallic appearance. Its brittleness is such that when subjected to stress or pressure greater than its endurance, it goes to pieces suddenly with a crash like glass. It has, therefore, been commonly supposed that amalgam is brittle, and consequently exhibits no other change under stress. Such conclusions are but natural, since no metal or other alloy exhibits these seemingly incompatible properties of *brittleness* and *ductility* at the same time. Iron is malleable and ductile, as is soft steel, but hardened steel and cast iron are exceedingly brittle. Neither iron nor any of its compounds could be possessed of both of these properties at the same time. Yet Dr. Black's experiments tend to show, as he says, that "in this particular the silver-tin amalgams seem to be an anomaly among the metallic compounds, for *they are at the same time both very brittle and very ductile.* If struck with a hammer, they fly to pieces; but if subjected to a comparatively light stress, either continuous or intermittent, they may be drawn out into thin laminæ or molded into any form without breakage".†

The resistance to stress in silver-tin amalgams made from freshly cut alloys increases very materially from

*Of "stress," Dr. Black, in the July, 1895, number of the Dental Cosmos, p. 554, says: "The stress in the ordinary use of the teeth has been shown to be from sixty to eighty pounds upon the area of two molars of medium size. This, if evenly distributed, would give from seven and a half to ten pounds on a filling occupying one-fourth the area of one of these teeth. This would be a filling of ordinary size; but it frequently happens that the filling must bear all of this stress, and occasionally such fillings must bear all of the stress that the person is capable of exerting. Therefore, while the filling itself may not have to endure a stress of more than seven and a half to ten pounds in chewing a piece of beefsteak, it is continually liable to have to bear the whole stress when some hard substance is caught upon it, or even the whole stress the person can exert. This may be anywhere from one to two hundred pounds, or even a greater stress in some cases."

†Dr. G. V. Black, Filling-materials, Dental Cosmos, xxxvii, p. 556.

the proportion of silver 40 and tin 60 which will withstand a stress of 178 pounds only, to that of silver 70 and tin 30, which withstands a stress of 316 pounds without breach of continuity. After this an increase of silver causes a decrease in resistance to stress. Amalgam made from annealed alloys shows a somewhat higher crushing strength, but these, like those made from freshly-cut alloys, show a decrease of crushing strength after 70 per cent of silver is passed. Five per cent of copper seems to increase the property of resisting stress more than any of the modifying methods used.*

**FLOW.**—The property which causes a substance to continue to yield under a stress without breach of continuity as long as the stress is maintained.

"The standard being sixty pounds for one hour on a cube 85x85x85 thousandths of an inch, * * * a pure silver-tin alloy may be said to flow from two and a half per cent to ten per cent, the difference depending on the composition of the alloy, the fineness of the cut, and the special mode of handling."†

Dr. Black, in explaining this property of amalgams, says: "When the flow has begun it continues as long as the stress is maintained. No increase of stress is required to maintain the flow;" that "it will go slowly with a light stress, somewhat quicker with a heavy stress, but it can not be made to go very quickly with a very heavy stress; it will break into fragments. A silver-tin amalgam is not malleable."‡ His conclusions, based upon further experiments with silver and tin separately, are, that this property can not be im-

*See tables, p. 368.
†Black: Filling-materials, Dental Cosmos, xxxvii, 566.
‡Ibid., p. 558.

parted by either of these metals, but results from the combination of the three—silver, tin and mercury; and further,* "that the strength of the mass depends mostly on the *perfect evenness of the distribution of the mercury.* Any irregularity in the work which disturbs this increases the flow," and even after distribution, "any form of violence weakens the product." Finely comminuted alloys flow more than coarsely divided ones.

The formula† of the alloy largely controls the flow of the amalgam, and is of vastly more importance than the percentage of mercury or the manner of manipulation, provided both of these be reasonable.

It will be noticed in alloys having a large content of tin that the percentage of flow is greatest.‡ For example, an amalgam made of the fresh-cut alloy silver 40 and tin 60, under the standard pressure of 60 pounds for one hour, flowed 40.15 per cent. Ageing the cut alloy seems to generally increase the flow of amalgams made from it. Thus, in the formula given above (silver 40, tin 60, annealed), the flow was 44.60 per cent. As a rule the annealed alloy makes a softer and tougher amalgam.

It will also be noted, by the tables, that the resistance to flow increases with the addition of silver, and that there is a notable increase in the resistance at sixty-five per cent, or, when we enter the group of hard alloys.

"The crushing strength," says Dr. Black, "proves to

*Black: Filling materials, Dental Cosmos, xxxvii, p. 561.

†N. K. Garhart states that an alloy containing as low as 45% of Ag, when properly manipulated and inserted in a cavity, will not flow to an appreciable degree.

‡See tables, p. 368.

be no test for the stability of an amalgam." All reasonable dental-amalgam alloys, when mixed with a "sufficiently low percentage" of mercury, are strong enough to withstand the stress of mastication. The flow, however, *is* an important test. The chief difficulty is, that while most of the alloys are capable of resisting the stress imposed, many of them will gradually change form under the same strain; thus, the appearance of the "black ditch" which is so often seen along the margin.

The chief influences which disturb the maintenance of size and form of an amalgam filling are contraction or expansion, and flow; therefore a minimum of these changes are the primary considerations in a satisfactory dental amalgam.

**EDGE STRENGTH** in an amalgam is the degree of resistance an edge or angle of an amalgam mass offers to force which tends to fracture it.

"Amalgams have heretofore been regarded as rigid crystalline masses, utterly devoid of malleability. The discovery of the existence of flow at once modifies all previous conceptions and data regarding edge strength, for it is evident that a corner or angle might not fracture, and yet flow under the stress of the impact of mastication, whereupon edge strength might be said to be great, and in reality be but slight. In view of the existence of the property of flow, edge strength must be measured as *rigidity*, the antithesis of flow, and a high crushing stress."*

**DISCOLORATION.**—The discoloration of amalgam fillings is for the most part due to the action of sulphuretted hydrogen. Silver and copper are readily at-

*Burchard: The American Textbook of Operative Dentistry, p. 224.

tacked by this gas, forming the black, insoluble sulphides of silver and copper. Amalgams containing a larger proportion of either are blackened from this cause, nor will those metals (such as gold or platinum) which are themselves untarnished by this agency, secure the same immunity to amalgams containing them. The sulphide of cadmium is lemon-yellow; hence amalgams containing this metal are discolored (as is the tooth structure) a light yellow.

**CONDUCTIVITY.**—As a conductor of thermal influence, says Dr. Burchard,* amalgam is midway between gold and the basic zinc cements.

**WASHING.**—Dental amalgams are frequently washed in alcohol, ether, or chloroform to remove oxides and oily matter attracted from the hand. It is, however, doubtful if such procedure gives any beneficial result. It has, however, been claimed that washed amalgams retain their color better.

*The American Textbook of Operative Dentistry, p. 226.

## CHAPTER XXII

## CLASSIFIED AMALGAMS

**Dental-amalgam alloys may be classified as BINARY, TERNARY, QUARTERNARY, QUINARY, Etc., according to the number of elementary constituents.**

**A BINARY DENTAL AMALGAM may be composed of mercury alloyed with any ONE of the various metals used as constituents of dental-amalgam alloys or dental amalgams, such as silver, tin, gold, copper, platinum, zinc, palladium, cadmium, bismuth, or antimony. COPPER and PALLADIUM, however, are the only ones which have thus far found any place of apparent usefulness.**

**SILVER** formed the prototype of binary dental amalgams, as it did of dental amalgams in general.

When finely divided, such as the precipitate, it readily and rapidly combines with mercury, evolving considerable heat, and forming a hard mass in a few seconds. In the state of larger particles, such as filings, it combines more slowly. According to Mr. Fletcher,* "The rapidity of combination is reduced by the use of a mixture of precipitated silver and filings. If the precipitate is in excess, and the mass is inserted before the hardening commences, there is a risk of bursting the tooth by the gradual expansion of the mass—[which Mr. Kirby claims amounts to 1/40 of the diameter of the plug] if a great excess of mercury is used

*Dental Metallurgy, p. 33.

the mass only partially hardens and the results are uncertain."

Silver, is, however, the most important and essential component of dental-amalgam alloys, and is usually the largest component of their composition. It unites chemically with mercury to form definite chemical compounds* having the varying formulæ of $Ag_6Hg$, $Ag_2Hg_3$, and AgHg. It is readily discolored by sulphur compounds.

**TIN** very readily combines with mercury, forming a friable, very slowly and imperfectly hardening amalgam. It is very probable that the action of tin and mercury when combined is a decided *contraction* of the mass. It has been stated by some that the mass expanded, and by others that it contracted, but accurate data are wanting. The author bases his opinion entirely upon the data furnished by Dr. G. V. Black.† In arriving at this conclusion, however, it is necessary to eliminate so many factors of influence, such as chemical affinities, fineness of cut of the alloy, manner of mix, manipulation, etc., that the opinion after all may seem of little value. The following notes of Dr. Black, rearranged, formed the data:

| Fillings, how Inserted | Formulae Fresh-cut | | Per cent of Mercury | How Mixed | Contraction = (—) Expansion = (+) Unit of Measurement 1 Thousandth of an inch | Amount of Contraction or Expansion if any |
|---|---|---|---|---|---|---|
| | Silver | Tin | | | | |
| Hand pressure | 70 | 30 | 46.36 | Hand | +.1,—.1 | Equalized |
| " " | 65 | 35 | 44.6 | " | Neither | Neutral |
| " " | 60 | 40 | 37.85 | " | —.05,+.1,—.05 | Equalized |
| " " | 42.45 | 57.55 | 37.27 | " | —.8, +.2,—.2 | —.0008 max'm |
| Burnished ... | 42.45 | 57.55 | 45.31 | Mortar | —.9, +.1 | —.0008 " |

*See p. 356.

†Contraction and Expansion of Silver-Tin Amalgams, Dental Cosmos, xxxvii, p. 648.

Tin and mercury show a disposition to unite—forming a definite chemical compound of a weak crystalline nature said to have the formula $Sn_2Hg$. It is second to silver in importance as a constituent of dental-amalgam alloys.

**GOLD** combines with mercury at any temperature, but more readily if either or both be heated slightly. Finely divided it combines even more rapidly. "Gmelin states that an amalgam of 6 of mercury to 1 of gold crystallizes in four-sided prisms, and that the mercury may be distilled off from this leaving the gold in the arborescent form."*

**COPPER** possesses the property of combining with mercury to form an amalgam which, on hardening or setting, may be softened by heat, kneaded, and inserted as a filling, and again becoming hard may be polished. It retains its metallic luster for some time when exposed to air, but blackens quickly when in contact with air or moisture containing sulphuretted hydrogen. Its peculiar properties have led to its introduction as a dental amalgam, first known as *Sullivan's Amalgam* or *Cement*. Its preparation and properties Mr. Fletcher describes as follows:† "Precipitate from a weak solution of sulphate of copper by rods of pure zinc. Wash the precipitated copper with strong sulphuric acid (the addition of a small quantity of nitrate of mercury assists greatly), and add mercury in the proportion of 3 copper to 6 or 7 mercury. This alloy has the property of softening with heat and again hardening after a few hours."

This amalgam has been thoroughly tried as a dental

*Makins' Metallurgy, p. 268.
†Dental Metallurgy, p. 60.

filling-material, and its use practically discontinued on account of the intense blue-black discoloration of its surface and the teeth containing it, and its undeniable surface disintegration. It has been thought to possess therapeutic value; indeed, Dr. Kirk says: "Its preservative quantities render it a valuable constituent in alloys for use in teeth of a low grade of structure." Of it Dr. Black says:* "This amalgam has so many good qualities that many abandon it with much regret. I think it generally acknowledged that copper amalgam fillings retain good margins, when they are once made good, better or more perfectly than any other filling-material." He shows that frequent reheating deteriorates the amalgam very materially; claims that it will not flow under stress and "within the limits of its strength it is as rigid as hardened steel;" that it *does not contract,* but exhibits very slight expansion on setting, and attributes the properties heretofore assigned to its therapeutic qualities to the fact that it simply seals the cavity more perfectly.

A variety of methods of preparing copper amalgam has been taught in the classrooms and described in our literature, some of which are as follows:

Dr. T. H. Chandler's method for making his "No. 1" and "No. 2" is as follows:†

No. 1. To a hot solution of sulphate of copper add a little hydrochloric acid, and a few sticks of zinc, and boil for about a minute. The copper will be precipitated in a spongy mass. Take out zinc, pour off liquor, and wash the copper thoroughly with hot water. Pour on the mass a little dilute nitrate of mercury, which will

*Copper Amalgam, Dental Cosmos, xxxvii, p. 737.
†Dental Chemistry and Metallurgy, Mitchell, p. 141.

instantly cover every particle of the copper with a coating of the mercury. Add mercury 2 or 3 times the weight of the copper, triturate slightly in a mortar, and finish by heating the mixture a few moments in a crucible.

No. 2. Take finely divided copper (copper dust) obtained by shaking a solution of sulphate of copper with granulated tin; the solution becomes hot, and a fine brown powder is thrown down. Of this powder take 20, 30 or 36 parts by weight and mix in a mortar with sulphuric acid, 1.85 specific gravity, to a paste, and add 70 parts of mercury, with constant stirring. When well mixed wash out all traces of acid and cool off. When used heat to 705° C. It can be kneaded like wax in a mortar.

**PLATINUM.**—"Worked platinum," says Mr. Makins,* "can not be amalgamated with mercury, and the only method of forming platinum amalgam consists in rubbing finely divided platinum (such as that reduced from the ammonio-chloride) and mercury together in a warm mortar; the combination of the two will be accelerated by moistening the two metals with water, acidulated with acetic acid."

**ZINC** readily amalgamates with mercury to form a very brittle amalgam, whatever may be the relative proportion. With large amounts of mercury it forms an amalgam similar to that of copper, but too brittle for dental use.

**PALLADIUM** may be precipitated from its solution by metallic iron or zinc. It should then be washed with weak nitric acid, and dried. This character com-

*Metallurgy, p. 304.

bines quite readily with mercury, attended by evolution of heat. It hardens quickly as it cools, but may be combined so as to set quickly or slowly, depending upon the proportion of its constituents. It turns very dark, but does not greatly discolor the tooth structure. On account of its quickly setting property it is difficult to work, and if inserted imperfectly it may harden so soon that it is almost impossible to remove it. Tombes says it shrinks less than any of the binary amalgams. The expensiveness of palladium has caused the use of this amalgam to be almost, if not entirely, discontinued.

Mr. Fletcher says:*

"It may be prepared to combine with mercury so as to set quickly or slowly by varying the strength of the solution; but it must be borne in mind that unless precipitated palladium sets very rapidly when mixed with mercury, it is totally useless for dental purposes; the plugs fail, unless fully hard, in so short a time, that the amalgam is difficult to insert whilst it remains plastic. Plugs of palladium amalgam generally contain about 70 to 80 per cent of mercury."†

**CADMIUM** forms a silver-white, somewhat brittle amalgam of a crystallo-granular texture, which under

*Dental Metallurgy, Fletcher, p. 41.

†Mr. Coleman in the subjoined gives his preparation of palladium amalgam: "About as much mercury as would fill the cavity to be treated is placed in the palm of the hand, and the palladium powder very gradually added. It requires some careful rubbing with the forefinger before the two become incorporated, when it should be divided into smallish pellets, and these rapidly carried one after another to the cavity, each piece being well compressed and rubbed into the inequalities of its walls by a burnishing or compressing instrument and with a rotary movement of the hand. This is continued until the cavity is quite filled. or even, if necessary, to some slight extent built out, the surface being rendered smooth and polished with a burnisher until it is quite set, which is generally in a very little (too short) a time."—*Dental Surgery and Pathology.*

He also states, according to Kirk, that it is probably the most durable of all amalgams, but the most difficult to manipulate. Its surface changes to a black color, but as a rule does not stain the structure of the tooth.—*Am. System of Dentistry.*

certain circumstances is said to be malleable, imparting that quality to its alloys.

**ANTIMONY AND BISMUTH.**—(See chapters on these subjects.)

**TERNARY DENTAL AMALGAMS.—These are generally alloys composed of SILVER and TIN,** comminuted by filing or turning in a lathe, and amalgamated into a coherent mass with mercury. The components are, as a matter of course, subject to considerable variation, the proportions of silver and tin ranging from 75 parts of the silver to 25 of the tin, to 40 of the silver and 60 of the tin. The proportions of mercury range from about 30 per cent of mercury to about 70 per cent of alloy, to equal parts by weight, or, exceptionally, a large proportion of mercury may be used. The comminuted alloy is amalgamated with the mercury by rubbing them together in the palm of the hand or in a Wedgwood or ground-glass mortar until a more or less smooth and coherent mass is formed. When a considerable amount of mercury is used in the mixing, the excess is generally squeezed out through a muslin cloth or chamois skin. The mass, when packed together, acquires a metallic hardness within a few hours, and arrives at its full degree of hardness usually in twenty-four to forty-eight hours. It is then a hard, brittle mass that may be dressed with a file and polished as other metallic bodies.

REQUISITE PROPERTIES OF A DENTAL AMALGAM

1. Permanency of Form (exhibiting as little tendency to *contract, expand* or assume a spheroidal form as possible).

2. Sufficient Density, Hardness, and Toughness to Resist Attrition.

3. Strength and Sharpness of Edge.

4. Complete resistance to the action of the Oral Secretions and Food.

5. Freedom from Admixture with any Metal Favorable to the Formation in the Mouth of Soluble Salts of an Injurious Character.

6. Good Color.

The first ternary dental-amalgam was that formulated by Dr. Townsend consisting of silver 42 and tin 58 parts. His formula has since been changed, however, to silver 44.5, tin 54.5, and gold 1. Investigations and experiments then seem to demonstrate that those alloys containing more than 50 per cent of silver gave better results. Later the scientific researches of Dr. Black* concerning the annealing of alloys gives evidence that the future ternary dental amalgam will closely approximate in formula silver 72.5 and tin 27.5.

By the table of dental-amalgam alloys submitted on page 364 it may easily be seen that silver and tin form the basis of all amalgams used in dentistry. With a view to overcoming the imperfections in and disadvantages of this simple ternary amalgam, and increasing its tooth-conserving qualities, and, therefore, its usefulness, a vast amount of experimentation has been carried on by the profession and the manufacturers. Papers after papers have been written, published, and discussed, all of which have had a tendency to prove that there is good reason to believe that the addition of small proportions of one or more other metals will, in a measure, overcome the objections inherent in an amalgam made of an alloy of silver and tin alone.

*See tables, p. 368.

**QUARTERNARY, QUINARY, ETC., DENTAL-AMALGAMS represent the basal alloy of silver and tin modified by the addition of one or more of the following metals in small proportions: Gold, platinum, iridium, copper, zinc, cadmium, bismuth, antimony, and aluminum.**

**GOLD** is usually added to silver-tin dental-amalgam alloys to the extent of from 2 to 7 per cent. Dr. Bonwill regards a greater quantity very undesirable.*

The addition of gold in the proportion of 5 per cent to an alloy of silver 61.75 and tin 33.25, says Dr. Black,† "seems to give a little softer working property, and slows the setting of the mass. The mass has something more of the pasty character, and the fillings made of the annealed alloy are apt to finish very soft, the surface being so springy that it is difficult to make a good finish. It takes a little less mercury than the unmodified alloy, and the flow is a little more. The amalgam is very tough, and bears a heavy stress before crushing. The shrinkage-expansion range is reduced three points."‡

Clinical records testify that it aids in maintaining a better color.

**PLATINUM.**—The use of platinum in dental amalgams was introduced by Thomas Fletcher.§ He claims for amalgams containing it in proper proportions, permanency of form, and the property of rapidly hardening, but admits that such are excessively dirty to

*Dental Cosmos, xxiv, p. 422.
†Dental Cosmos, xxxviii, p. 988.
‡See table, p. 368.
§Dental Metallurgy, Fletcher, p. 39.

mix in the hand. Dr. Essig says it impairs an amalgam of silver and tin.*

"The appearance of the mass made of this alloy [silver 61.75, tin 33.25, and platinum 5] is very remarkable. That from the fresh cut alloy is fairly white, but that from the annealed alloy is dark, and, in kneading, blackens the hand to an extraordinary degree with a grayish-blue black that is rather difficult to remove. The mass looks dirty and the finished filling is dark. The mass has a very peculiar softness to the feel under the instrument. The setting is slowed considerable. It flows badly. The shrinkage-expansion range is increased, and lies a little higher in the scale."†

"When platinum is combined with silver, tin, and gold, its influence becomes apparent," explains Dr. Essig:‡ "With the proper proportion of mercury, it seems to confer upon such an alloy the property of almost instantly setting, as well as much greater hardness. Thus, it will be seen, that the qualities claimed for platinum *per se* belong in reality to the combination of tin, silver, gold, and platinum with mercury, since, if either one of the others is omitted, the platinum does not remain passive, but actually by its presence causes marked deterioration of qualities essential in a dental amalgam."

Dr. Black's experiment upon such an amalgam demonstrates it as being very little better than the previous one:

Silver .....44.81,
Tin .....52.78,
Gold ..... 1.78,
Platinum..... .62, and Mercury 39.18 *per cent*

*Dental Metallurgy, Essig, p. 52.
†Black: Dental Cosmos, xxxviii, p. 988.
‡Dental Metallurgy, p. 54.

Mixed in the hand and inserted by hand pressure. Margins open all around from .0003 to .0008 of an inch. The same alloy with 37.45 mercury showed a flow of 19.81, and crushing strength of 225 pounds.

**COPPER.**—A very large percentage of the alloys found upon the market contains small proportions of copper, ranging usually from 3 to 8 per cent.

With tin, copper yields a very white amalgam, by proper manipulation. There is, however, a tendency to soon discolor, which may be controlled, it is said, by a small proportion of gold.

Of the alloy of silver 61.75, tin 33.25, and copper 5, Dr. Black says: "The fresh-cut, sets very quickly. The mass makes up soft, but it becomes hard almost immediately after it is left to itself. The annealed alloy makes a very soft, pleasant-working mass, and the setting is as slow as in the unmodified alloy. Expansion and the expansion-shrinkage range is markedly increased, the flow is diminished, and the crushing stress is the greatest of the series."*

**ZINC** 5, silver 61.75, and tin 33.25, Dr. Black says, forms† "a very remarkable amalgam for the amount and slowness of its expansion * * * in the fresh-cut alloy the expansion continued forty days, [reaching .0068 of an inch]. The expansion in the filling from the annealed alloy [.0009] was not completed until thirty days had elapsed." He further explains that the mass is remarkable for its adhesion to the walls of the cavity; sets very quickly; that the zinc decreases the flow to the least of any of the series of amalgams examined (fresh-cut 1.83, annealed 2.07 per cent); that

*Dental Cosmos, xxxviii, p. 988.
†Ibid., xxxviii, p. 989.

the filling has good resistance (290 and 345 pounds); and requires more mercury than the unmodified alloy of silver 65 and tin 35.

When zinc is added to silver, tin and gold alloys, it is said to prevent discoloration to a considerable extent.

The addition, however, makes the amalgam "coarse-grained" and more difficult to amalgamate. "Front-tooth alloys" usually contain zinc to maintain their whiteness. "A 'facing'—approximately, tin 55, silver 37, gold 5, zinc 3,—is that which at present is least liable to discolor."*

Zinc is also added to amalgam alloys of silver, tin, and copper, but presents an amalgam little different from the above.

**BISMUTH.**—An alloy of silver 61.75, tin 33.25, and bismuth 5 is remarkable for the readiness with which it amalgamates with mercury, and the small amount of mercury it requires. The working property of the amalgam is soft, the mass springy and very dark, the expansion and shrinkage range reduced, the flow increased, and the resistance to crushing reduced.

**ALUMINUM.**—Dr. Black states† that alloys containing 5 per cent of aluminum evolve considerable heat while setting, expand enormously, oxidize readily, and that a distinct crackling of gas-disengagement is heard during their packing. "The formation of aluminum amalgam is characterized by an exhibition of the affinity of aluminum for oxygen. Aluminum oxide is doubtless formed, which increases the volume of the amalgam mass."

**Cadmium,** as a component of dental-amalgam alloys,

*Flagg: Plastics and Plastic Fillings, p. 104.
†Dental Cosmos, xxxviii, p. 990.

has been very unsatisfactory, and should never be used. (See chapter on Cadmium.)

For **antimony** see chapter devoted to that metal.

**ANALYSIS OF DENTAL AMALGAMS.**—A perfect familiarity with the composition of the alloys used in individual practice is indispensable, and it is also important, and, at times, exceedingly desirable, to be able to determine the composition of other alloys or old amalgam plugs.

Analysis is accomplished by two means, known respectively as the dry and wet methods.

**The Dry Method** consists principally of two parts:

1. *A physical examination,* noting *weight, color* of alloy, and discoloration, if any, and *hardness.*

2. Subjection to the *heat* of the *blowpipe* either alone or in the presence of certain reagents.

**The Wet Method** generally consists of dissolving the solid in some solvent, and precipitating the dissolved constituents separately as the simpler compounds of oxygen, sulphur, chlorine, etc.

Before proceeding with the analysis of an old amalgam plug by the wet method, a careful study should be made of its *weight, color, discoloration, hardness,* etc.

**MERCURY.**—It may then be weighed and placed in a hard glass tube or porcelain crucible and heated to a red heat, to drive off the mercury, the amount of which is determined by the difference in the first weight and that obtained after heating.

This method is somewhat inaccurate, on account of the oxidation or volatilization of some of the constituents.

The plug deprived of its mercury is placed in a mortar and finely divided; then a weighed quantity (usually

10 or 20 grains) is transferred to a glass flask and sufficient chemically pure nitric acid added to more than dissolve it, by the aid of gentle heat.

The powdered condition of the alloy is necessary otherwise the metastannic acid formed by the action of nitric acid upon the tin, after a few moments, so protects the surface of the alloy, that it greatly retards, if not in a measure prevents, its complete solution.

Much can be discerned qualitatively by the appearance of the solution. After the action of the acid is completed, there will appear a residue in the bottom of the flask, with a clear supernatant liquid. If this liquid is colored a greenish-blue, *copper* is present. If the precipitated metastannic acid is white, or nearly so, gold and platinum in any considerable quantity need not be expected, as the presence of a very small amount of *gold* is sufficient to tint the metastannic acid purple, due to the formation of the *purple of Cassius;* and the presence of *platinum* is determined by a black powder, small particles of metallic platinum mixed with the metastannic acid. Very small quantities of this metal are, however, dissolved in nitric acid, in the presence of a large excess of silver.

**TIN.**—The contents of the flask should then be filtered, the filtrate preserved, and the precipitate thoroughly washed with distilled water, dried, the metastannic acid ($H_{10}Sn_5O_{15}$) rendered anhydrous ($SnO_2$) by calcining at a red heat, and then weighed,—78.66 per cent of the mass representing the amount of tin in the alloy.

**ANTIMONY.**—If there be any reason to suspect the presence of antimony in the alloy, the dioxide of tin ($SnO_2$) should be fused in a silver crucible with sodium

hydrate (NaHO) by which the antimonate ($NaSbO_2$) and stannate ($Na_2SnO_3$) of sodium are formed. The fused mass is now digested and disintegrated in cold water, and filtered. If antimony be present, it will be caught on the filter paper as the antimonate of sodium, while the soluble stannate of sodium passes through with the filtrate. The antimonate should now be washed with distilled water, dried and weighed—68.92 per cent of the mass representing the amount of antimony in the alloy.

**SILVER.**—The filtrate which was originally the supernatant liquid in the flask, should now be diluted somewhat, and hydrochloric acid added until no more precipitate (silver chloride) is formed, when the whole should be filtered, the precipitated silver chloride remaining on the filter paper, washed with distilled water, dried and weighed—75.26 per cent of the mass representing the amount of silver present in the alloy.

**COPPER.**—The original supernatant liquid in the flask is now treated to sulphuretted hydrogen. The copper and cadmium are thrown down as sulphides. The copper sulphide is black, while that of cadmium is lemon yellow. The contents of the flask are again filtered, and the copper and cadmium sulphides caught upon the filter paper; these are washed with distilled water and treated with dilute sulphuric acid, the cadmium sulphide being dissolved. All is again filtered; the dissolved cadmium sulphide passing through, and the copper sulphide remaining upon the filter, should be washed, dried, and weighed—66.49 per cent of the mass representing the amount of copper present in the alloy.

**CADMIUM.**—The cadmium sulphide may be thrown

down now with potassium hydrate as cadmium hydroxide, Cd2HO, dehydrated by heating, and weighed as cadmium oxide, CdO—87.49 per cent of the mass representing the amount of cadmium in the alloy.

**ZINC.**—From the original solution the zinc may be separated as the carbonate ($ZnCO_3$) by adding one of the alkaline carbonates. It is then washed, heated to redness, and weighed as the pure oxide of zinc, ZnO—80.24 per cent of the mass representing the amount of zinc in the alloy.

**GOLD.**—Probably the most practical manner of determining the amount of gold in a dental-amalgam alloy of approximately unknown composition is as follows: After drying and accurately weighing the insoluble residue of metallic platinum and precipitated compounds of gold and tin, obtained upon dissolving the original alloy or plug in pure nitric acid, it should be fused with potassium carbonate and cyanide; the tin oxide is dissolved by the flux, and the resulting button is composed of gold and platinum. This should now be rolled to a very thin ribbon, cut up and digested in *aqua regia* (see chapter on gold), forming the soluble chlorides of gold and platinum. The chlorides thus formed are then dissolved in a sufficient quantity of distilled water, from which the gold is precipitated in the metallic state by the addition of a solution of oxalic acid or the sulphate of iron. It is then collected by filtration, fused, and weighed.

**PLATINUM.**—The platinum in the remaining solution is thrown down as ammonio-platinic chloride $(H_4NCl)_2\ PtCl_4$, by the addition of sal ammoniac, washed, dried, and weighed as such—44.17 per cent of the mass representing the amount of platinum in the alloy.

# LABORATORY PROCEDURE

## FOR STUDENTS

IN

## DENTAL METALLURGY

BY

J. D. HODGEN, D.D.S.

## APPARATUS REQUIRED BY EACH STUDENT

1. 1 Beaker, 320 c.c.
2. 1 Beaker, 250 c.c.
3. 1 Florence flask, 500 c.c.
4. 1 Funnel, 100 mm.
5. 4 Test tubes, 13 mm.
6. 8 Test tubes, 18 mm.
7. 2 Flint bottles, 150 c.c.
8. 1 Flint bottle, 250 c.c.
9. 1 Graduate, 120 c.c. (double graduation).
10. 1 Tumbler.
11. 1 Piece Glass stirring rod.
12. 1 Porcelain evaporating dish, 150 c.c.
13. 1 Test tube rack.
14. 1 Test tube brush.
15. 1 Crucible-tongs, 25 cm.
16. 1 Sand-bath, 100 mm.
17. 1 Test tube holder.
18. 1 Iron ladle.
19. 1 Bunsen burner.
20. 1 Ring-stand, 2 rings.
21. 1 Tripod.
22. 6 Crucibles.
23. 1 ft. White rubber tubing.
24. 1 Cork for Florence flask.
25. 1 Cork for flint bottle.
26. 1 Cork for 13 mm. test tube.
27. 1 Cork for 18 mm. test tube.
28. 50 Strips Litmus.
29. 50 Labels.
30. 50 Filter papers 15 cm., ½ pkg.
31. 1 Rule (double graduation).
32. 1 Blowpipe, 25 cm.
33. 1 Small towel.
34. 50 Pieces paper about 20 cm. square.
35. 1 Note book.
36. 1 Small padlock.

## PERIOD I
## ASSIGNMENT OF LOCKERS

Students will be admitted in the laboratory, for the selection of lockers, in accordance with the number of their Laboratory Fee Receipt. No assignment will be made to any student until such receipt is presented to the Instructor.

Place articles "furnished by student" on bench for inspection by Instructor. After inspection, take all articles out of locker and placed on bench and place all articles "furnished by student" in locker.

Instructor will read "Requirements" for each student, reserving the articles to be washed until the last, and as he reads, each student will replace the article called in the locker, thereby seeing that every article is present and in good condition. If any are missing, they must be supplied before the close of the period.

All glass apparatus must be thoroughly washed and wiped before replacing in the locker, and when invoice is completed student will place his own lock on the locker and retire from the laboratory after handing to the Instructor his Roll Number and Locker Number.

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## PERIOD II
## PROPERTIES OF METALS

INSTRUCTOR EXPLAIN the use of each article of the student apparatus.

INSTRUCTOR EXHIBIT and briefly describe each metal, of importance in dental metallurgy, together with its ore, which are to be replaced in the Metallurgical Museum for inspection at any time.

EXPERIMENT No. 1: SPECIFIC HEAT. Prepare bullets of exactly equal weights of several of the above metals, such as zinc, silver, cadmium, tin and lead; expose them to the same temperature, for the same length of time, and then drop them simultaneously upon a thick sheet of wax placed across an open

side of a pasteboard box. They will be observed to melt their way through or into the wax in the order named.

(Performed by Instructor.)

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## PERIOD III

## COMPOUNDS OF METALS AND NONMETALS

APPARATUS—Bunsen burner, iron ladle, ring stand, funnel, filter paper, evaporating dish, beaker, litmus paper.

REAGENTS—Lead, Copper, Nitric Acid, Potassium, Potassium Hydrate, Zinc Sulphate, Ammonium Hydrate, Ferric Chloride, Magnesium Hydrate, Ferrous Sulphate.

EXPERIMENT No. 2: OXIDATION OF SODIUM. With a knife cut off a small piece of metallic sodium; observe it exhibits a brilliant luster but speedily tarnishes by combining with the oxygen of the air, forming the oxide (NaO) of sodium. Plunge the sodium into a jar of oxygen: it takes fire and burns with a brilliant yellow flame.

(Performed by Instructor.)

EXPERIMENT No. 3: OXIDATION OF ZINC. With a piece of zinc foil form a tassel, gently warm the end, dip into flowers of sulphur, kindle, and let down into a jar of oxygen, when the flame of the burning sulphur will ignite the zinc, which burns with great brilliancy, forming oxide of zinc (ZnO).

(Performed by Instructor.)

EXPERIMENT No. 4: REDUCTION BY HYDROGEN. Pass the delivery tube of an ordinary hydrogen generator (A, Fig. 1) into one end of a drying tube (B), well filled with fragments of calcium chloride, for the purpose of absorbing the moisture which may be carried over with the gas; connect the other end of the drying tube with a tube (C) upon which a bulb (D) has been blown for the reception of the metallic oxide. After the gas has completely driven the air out of the apparatus, heat is applied to the bulb containing the oxide. As the dry hydrogen flows over the heated oxide in a strong stream it com-

bines with the oxygen—favored by heat—and passes out of the tube (E) as aqueous vapor, while the metal is left free.

(Performed by Instructor.)

EXPERIMENT No. 6: ACID FORMING OXIDE. Place two grams of sulphur in a deflagration spoon, ignite and hold in a flint bottle containing 50 c.c. of water; when sulphur is burned, remove deflagration spoon, cork the bottle, shake well and test with litmus.

(Performed by Instructor.)

EXPERIMENT No. 7: BASIC OXIDE. Oxidize five grams metallic lead in an iron ladle, over Bunsen flame; dissolve in water and test with litmus.

EXPERIMENT No. 8: HYDROXIDE. Place a small piece of potassium on 100 c.c. of water in a beaker; note liberated hydrogen is ignited. Test with litmus.

EXPERIMENT No. 9: FRESH HYDRATED OXIDE OF IRON. (Antidote for arsenic.)

(a) Add ammonium hydrate to 10 c.c. of ferric chloride in a beaker; wash ppt. until entirely freed from ammonia.

(b) Add magnesium hydrate to ferric sulphate. (To be used immediately without washing.)

EXPERIMENT No. 10: OXIDES BY ACTION OF ALKALIES OR ACIDS. Produce zinc oxide from soluble zinc sulphate ($ZnSO_4$) by action of potassium hydroxide (KOH) and dry precipitate by heating.

Produce cupric oxide by digesting metallic copper in nitric acid and then strongly heating the copper nitrate thus formed.

EXPERIMENT No. 11: TESTS FOR METALLIC SALTS IN SOLUTION. To the following salt solutions in several test tubes add a few drops of sulphuretted hydrogen.

| | | | |
|---|---|---|---|
| $Pb(C_2H_3O_2)_2$ + | $H_2S$ = | $PbS$ + | $2HC_2H_3O_2$ |
| Lead acetate | | Lead sulphide (Black) | |
| $2AsCl_3$ + | $3H_2S$ = | $As_2S_3$ + | $6HCl$ |
| Arsenous Chloride | | Arsenous Sulphide (Lemon-yellow) | |

| | | | |
|---|---|---|---|
| $Cd(NO_3)_2$ + Cadmium Nitrate | $H_2S$ = | CdS + Cadmium Sulphide (Yellow) | $2HNO_3$ |
| $2SbCl_5$ + Antimonic Chloride | $5H_2S$ = | $Sb_2S_5$ + Antimonic Sulphide (Orange-yellow) | 10HCl |
| $Zn(C_2H_3O_2)_2$ + Zinc acetate | $H_2S$ = | ZnS + Zinc sulphide (White) | $2HC_2H_3O_2$ |
| $HgCl_2$ + Mercuric chloride | $H_2S$ = | HgS + Mercuric sulphide (1st White) (2nd Yellow-Orange) (3rd Brown) (4th Black) | 2HCl |

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## PERIOD IV

## LINING FIRE BOXES: HANDLING CRUCIBLES

APPARATUS: Mixing basins, large (beer) bottles, crucibles, small flat stick 12 inches long, Asbestos, Silex, Fire Clay (¼ Fire Clay—¾ Silex—Asbestos ad lib.)

STUDENTS INSTRUCTED how to use furnaces.

REFRACTORY FURNACE BOX LINING. A place at the furnace will be assigned to two or three students in common, and they will make for their use, under the direction of the Instructor, a refractory fire box lining of clay and asbestos. This will be under the care of the students assigned during the year, who will see that no fluxes are spilled or dropped therein.

Remove blowpipe and see that all parts are in perfect working order.

Remove all debris from fire box.

Moisten the bottom and sides of fire box thoroughly.

Place beer bottle in center of fire box, place tip of blowpipe against the bottle firmly, then pack lining material all around the bottle allowing it to extend ½ inch above top of furnace box.

Remove bottle carefully; place layer of lining material ½ inch thick in bottom of fire box, then place in center an inverted base of a crucible so that top of the base of the crucible will be level with the top of blowpipe.

Smooth sides, top and bottom perfectly and then dry with slow fire.

Make cover of same lining material and let stand without heating until next period.

EXPERIMENT: BORAXING CRUCIBLES. Each student will proceed to borax a crucible under the verbal direction of the Instructor. Preserve crucible.

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## PERIOD V
## ELECTRIC FURNACES

Instructor will give a clinical demonstration of method of making muffle for electric furnace and method of wiring same.*

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## PERIOD VI
## METALLURGY OF LEAD

APPARATUS: Mouth blowpipe, willow charcoal block, test tubes, asbestos board, tripod, ring stand, funnel, filter paper.

REAGENTS: Lead monoxide, red lead, nitric acid, dilute sulphuric acid, hydrochloric acid, lead foil.

EXPERIMENT No. 13: REDUCTION. Heat on charcoal block under the R. F. about 1 gm. of lead monoxide (litharge) and obtain a metallic globule of lead. Afterwards scrape charcoal block clean with as little injury to it as possible.

EXPERIMENT No. 14: LEAD DIOXIDE. To about 1 gm. of red lead placed in a t. t. add 10 c. c. of dilute nitric acid. The lead monoxide is dissolved and the lead dioxide (chocolate colored) remains. Dilute and filter.

EXPERIMENT No. 15. On asbestos board placed on tripod, heat 1 gm. of lead monoxide in the presence of air—red lead.

*See Electric Furnace, p. 100.

(Note—The product soon loses its additional oxygen when heated but for a short time, returning to the lead monoxide.)

EXPERIMENT No. 16: ACTION OF SULPHURIC ACID ON LEAD. (a) To a small piece of lead foil in a t. t. add dilute sulphuric acid, note action, if any.

(b) Pour out the dilute sulphuric acid, and add concentrated sulphuric acid to same foil. Note action. What is formed? Write reaction.

EXPERIMENT No. 17: ACTION OF NITRIC ACID ON LEAD. To a small piece of lead foil in a t. t. add a small quantity of dilute nitric acid and warm. Note action. What is formed? Write reaction.

EXPERIMENT No. 18. ACTION OF HYDROCHLORIC ACID ON LEAD. To a small piece of lead foil in a t. t. add a small quantity of strong hydrochloric acid and boil. Note action. What is formed? Write reaction.

EXPERIMENT No. 19: TESTS OF LEAD IN SOLUTION. To a small amount of lead salt solution add the following reagents: Sulphuretted hydrogen, potassium hydroxide, ammonium carbonate, sulphuric acid, hydrochloric acid. Note action, character, color and solubility of ppt.

EXPERIMENT No. 20: LEAD-TREE EXPERIMENT. Dissolve 4 grams of the nitrate or acetate of lead in about 240 c. c. of distilled water and put the solution in a bottle. Suspend a piece of sheet zinc or a spiral of zinc wire in the center of the solution and let it stand. The lead will be deposited slowly in a crystalline form, known as *arbor plumbi.* At the same time the zinc will pass into solution, the lead simply replacing the zinc. Next period after the tree has been formed, filter off some of the solution and see whether or not zinc is contained in it. There will probably be some lead left. In order to detect the zinc, the lead will have to be removed. This may be done by adding sulphuric acid (forming the sulphate) and alcohol (to prevent its being redissolved). Filter off the lead sulphate, and to the filtrate add just enough *ammonia* to neutralize the *sulphuric acid,* and then test with *ammonium hydro-sulphide;* white zinc sulphide is precipitated.

NOTE—First part of this experiment is to be performed during this period. The last part during Period XI, on zinc.

SOLDERING "IRON". Furnish each student with one piece of copper wire ½ inch in diameter, 2 inches long, with ⅛ inch hole drilled and tapped ½ inch deep in one end; and one piece of steel wire 3/16 inch in diameter, 6 inches long, threaded to fit the copper. Student will point copper, make wooden handle, assemble parts and present to instructor at next period.

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## PERIOD VII

## METALLURGY OF LEAD—CONT'D

APPARATUS: Ingot molds, balances, iron ladle, evaporating dish, soldering "iron".

REAGENTS: Lead, tin, zinc, hydrochloric acid, ammonium chloride, rosin, brick, sheet tin.

EXPERIMENT No. 21: ALLOYS. Make an ingot model of lead and tin, (parts dictated to each student by Instructor) exactly 7 mm. (or as permitted by ingot mold) thick, 11 mm. wide, 45 mm. long, and shaped like model presented by Instructor.

When cold, clean, polish, and scratch neatly on one surface: formula and weight, before and after melting. Student preserve until end of term.

EXPERIMENT No. 22: SOLDERING SOLUTIONS. Make solution of zinc chloride by adding sheet zinc to hydrochloric acid in evaporating dish.

EXPERIMENT No. 23: SOFT SOLDERING. Endeavor to solder two pieces of metal previous to tinning the copper. Demonstrate the use of zinc chloride, resin with brick and ammonium chloride for tinning the "copper."

EXPERIMENT No. 24: Tin the soldering "iron", using solder and zinc chloride previously prepared. Solder two strips of zinc using hydrochloric acid as a flux. Solder two strips of tin using rosin as a flux.

EXPERIMENT No. 25: Cut sheet tin into pieces 4x5 inches, cut out corners and fold, so as to make tin box 3 inches long, 2 inches wide and 1 inch deep. Solder corners with soldering "iron" and soft solder previously prepared.

# PERIOD VIII
## METALLURGY OF TIN

APPARATUS: Funnel, filter paper, ring-stand, test tubes, labels, evaporating dish.

REAGENTS: Hydrochloric acid, sulphuric acid, nitric acid, sodium hydrate, ammonium hydrate, hydrogen sulphide, stannous chloride, stannic chloride, tin foil.

EXPERIMENT No. 26: ACTION OF SULPHURIC ACID ON TIN. (a) To a small piece of tin foil in a t. t. add concentrated sulphuric acid. Note action carefully. (b) To a small piece of tin foil in a t. t. add dilute sulphuric acid. Note action. What is formed? Write reaction.

EXPERIMENT No. 27: ACTION OF NITRIC ACID ON TIN. (a) To a small piece of tin foil in a t. t. add concentrated nitric acid and heat. What is formed? Write reaction. (b) To a small piece of tin foil in a t. t. add dilute nitric acid. What is formed? Write reaction.

EXPERIMENT No. 28: ACTION OF HYDROCHLORIC ACID ON TIN. To several small pieces of tin foil in a t. t. add a little concentrated hydrochloric acid and boil carefully. (Let there be more tin than will dissolve.) What is formed? Write reaction. Label and preserve.

EXPERIMENT No. 29: ACTION OF AQUA REGIA ON TIN. To a small piece of tin foil in a t. t. add a little hydrochloric acid and less of nitric acid. What is formed? Write reaction. Label and preserve. Be careful of the fumes.

EXPERIMENT No. 30: ACTION OF CAUSTIC ALKALIES ON TIN. To a small piece of tin foil in a t. t. add sol. of sodium hydrate (or potassium hydrate) and boil. What is formed? Write reaction.

EXPERIMENT No. 31: TESTS FOR TIN IN SOLUTION. To small amounts of tin salt in solution (stannous chloride preserved) add the following reagents: sodium hydrate, (or potassium hydrate), ammonium hydrate, hydrogen sulphide, gold chloride. Note action, character, color, solubility, etc., of the ppt.

## PERIOD IX
## METALLURGY OF TIN—CONT'D

APPARATUS: Ingot molds, balances, ladle, test tube.

REAGENTS: Potassium bitartrate, stannous chloride, sheet copper, tin foil, tin, lead, copper, antimony, bismuth, silver, gold.

EXPERIMENT No. 32: ALLOYS. Make an alloy assigned by Instructor. All alloys to be hereafter made, must be 7x11x45 mm., well polished, and on one surface the formula and weight before and after melting, neatly scratched.

EXPERIMENT No. 33: DEPOSITION OF TIN. Place in a t. t. a small piece of clean sheet copper, or any brass or copper article, such as crown or bridge, between tin foil, and add a saturated solution of acid potassium bitartrate, adding a little stannous chloride, and boil for several minutes.

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## PERIOD X
## METALLURGY OF BISMUTH

APPARATUS: Bunsen burner, charcoal, blowpipe, ladle, ingot molds, test tubes, balances.

REAGENTS: Sodium carbonate, solutions of hydrogen sulphide, sodium hydrate, potassium carbonate, water, tartaric acid, bismuth, bismuth subnitrate, lead, tin, antimony, cadmium.

EXPERIMENT No. 35: REDUCTION OF BISMUTH. Heat with blowpipe 5 dgm. of bismuth subnitrate with an equal amount of sodium carbonate, on a charcoal block. Examine carefully the metallic globule as to appearance, malleability, hardness, etc.

EXPERIMENT No. 36: TESTS FOR BISMUTH SALT IN SOLUTION. To small amounts of bismuth nitrate solution in a t. t. add the following reagents, and note the changes, if any: hydrogen sulphide, sodium hydrate, potassium carbonate, water. To the ppt. formed by water add tartaric acid, this will distinguish bismuth from antimony, by the water test alone.

EXPERIMENT No. 37: ALLOYS OF BISMUTH. Students will make one of the following alloys, as assigned by the

Instructor. Calculate accurately the amount of metal needed to make the required size ingot, that none be wasted.*

| ALLOY | Bismuth | Lead | Tin | Antimony | Cadmium |
|---|---|---|---|---|---|
| Newton's . ..... | 8 | 5 | 3 | .. | .. |
| Rose's F. A. 1..... | 2 | 1 | 1 | .. | .. |
| Rose's F. A. 2..... | 8 | 8 | 3 | .. | .. |
| Wood's ..... | 6 | 4 | 2 | .. | 2 |
| Onion's . ..... | 5 | 3 | 2 | .. | .. |
| "La Nation" . ... | 48 | 19 | 26 | .. | 13 |
| Hodgen's . ..... | 8 | 5 | 3 | 2 | .. |
| Mathew's . ..... | 48 | .. | 19 | .. | 13 |
| Darcet's 1 ..... | 7 | 2 | 4 | .. | .. |
| Darcet's 2 . ..... | 16 | 4 | 7 | .. | .. |
| Darcet's 3 . ..... | 8 | 6 | 2 | .. | .. |

## PERIOD XI

## METALLURGY OF ZINC

APPARATUS: Bunsen burner, test tubes, ring stand, filter paper, funnel, evaporating dish, sand bath, tripod.

REAGENTS. Zinc, zinc oxide, arsenous oxide, sulphuric acid, hydrochloric acid, sodium hydrate, sodium carbonate, ammonium sulphide, hydrogen sulphide, sodium phosphate, meta-phosphoric acid, nitric acid.

EXPERIMENT No. 38: ACTION OF HYDROCHLORIC ACID ON ZINC. To a small piece of zinc in a test tube add about 5 c. c. of dilute hydrochloric acid. Write reaction. Save for experiment No. 40.

EXPERIMENT No. 39: PREPARATION OF ZINC OXIDE BY ACTION OF NITRIC ACID ON ZINC. To about 20 grams of zinc in an evaporating dish add sufficient nitric acid in small quantities (50% sol.) to dissolve.

(Perform this exp. in fume chamber.)

When zinc is in solution, place evaporating dish on sand bath and evaporate to dryness. Save oxide till next period.

EXPERIMENT No. 40: TEST FOR ZINC SALT IN SO-

*Mold for Bismuth Alloys: Prepare sectional mold from natural tooth, with plaster of Paris, and pour bismuth alloy into same to show accuracy in copying fine lines. 8 grams gross weight is sufficient of this alloy.

LUTION: To a zinc salt in solution add the following reagents and note results: sodium hydrate, sodium carbonate, ammonium sulphide, hydrogen sulphide.

EXPERIMENT No. 41: Filter about 15 c. c. of the solution saved from experiment 20 "Metallurgy of Lead," Period VI. To the filtrate add, drop by drop, sulphuric acid till no more lead sulphate is thrown down. Filter again to remove the sulphate of lead and test the filtrate for zinc in solution. NOTE: If all the lead is not removed, its presence will interfere with the test for zinc.

EXPERIMENT No. 42: TEST FOR ARSENIC IN ZINC OXIDE. (a) Into a t. t. containing 5 c. c. of water place 5 dgm. of zinc oxide and a very small quantity of arsenous oxide (about as much as is used in pulp devitalization). Now add a few drops of hydrochloric acid and boil. A little hydrogen sulphide will throw down a lemon-yellow ppt., the sulphide of arsenic.

(b) Into a t. t. containing 5 c. c. of water, place 5 dgm. of zinc oxide and a few drops of hydrochloric acid, and boil. Test for the presence of arsenic.

EXPERIMENT No. 43: Test zinc for malleability at ordinary temperatures; when heated to from 100° to 150° C.; and also at 205° C.

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## PERIOD XII

## METALLURGY OF ZINC—CONT'D

APPARATUS: Crucibles, ingot mold, mortars, bolting cloth, evaporating dish, sand bath, tripod, stirring rod, mixing slab, spatula, balances.

REAGENTS: Old oxidized zinc, pulverized charcoal, stick of wood, zinc oxide, metallic zinc, pigments, metaphosphoric acid, zinc chloride.

EXPERIMENT No. 44: BASIC ZINC CEMENT POWDER. Calcine in a crucible, at white heat (or as near as possible) for two hours, a small quantity of zinc oxide. Powder in a mortar, bolt through cloth, color with pigments, and preserve.

EXPERIMENT No. 45: Calcine in a separate crucible, as

above the zinc oxide prepared at last period by action of nitric acid ($HNO_3$) on zinc.

Powder in a mortar, bolt through cloth and preserve.

EXPERIMENT No. 46: DEOXIDIZING ZINC. Melt old partially oxidized zinc in a crucible, and when molten, cover the surface with pulverized charcoal: heat at a strong temperature, and stir with a stick of wood. After a few minutes the zinc may be poured, and will be found to be quite free of the oxide.

EXPERIMENT No. 47: ZINC OXIDE. Prepare a small quantity of zinc oxide by heating metallic zinc to about 918° C. in an open crucible.

EXPERIMENT No. 48: PHOSPHORIC ACID FOR CEMENT. Place 10 c.c. of orthophosphoric acid in an evaporating dish, then add aluminum phosphate to the point of saturation.

NOTE: On cooling, the liquid thickens—the flame should, therefore, be removed a little before the desired consistence is attained. Mix with powder of experiment 44 as in mixing cement.

EXPERIMENT No. 49: ZINC CHLORIDE FOR CEMENT. Deliquesce 10 grams of zinc chloride with a very small quantity of distilled water. Warm slightly and cool. Mix with powder to form oxychloride of zinc—ZnClHO.

EXPERIMENT No. 50: Make a mix of the calcined zinc oxide (commercial) and the cement liquid prepared from modified phosphoric acid (experiment 48). Preserve.

EXPERIMENT No. 51: Make a mix of the calcined zinc oxide (obtained through precipitation, experiment 39) and the cement liquid prepared from modified phosphoric acid (experiment 48). Preserve.

Make a comparative test of above mixes, noting solubility and permeability.

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## PERIOD XIII

## METALLURGY OF COPPER

APPARATUS: Crucibles, ingot molds, stirring sticks, test tubes, knife.

REAGENTS: Copper, zinc, tin, aluminum, nickel, borax,

sodium hydrate, potassium hydrate, ammonia, potassium ferrocyanide, potassium ferricyanide, zinc plate strip.

EXPERIMENT No. 52: The student will prepare some one of the following alloys, as directed by the Instructor:

| ALLOYS | Copper | Zinc | Tin | Nickel |
|---|---|---|---|---|
| Sheet brass.....(must be rolled).. | 68 | 32 | .. | .. |
| Wire brass.....(must be drawn).. | 71 | 29 | .. | .. |
| Oreide . ..... | 68 | 13.5 | 0.5 | .. |
| Dutch Metal . ..... | 11 | 2 | .. | .. |
| Pinchbeck . ..... | 88 | 12 | .. | .. |
| Mosaic gold . ..... | 5 | 5 | .. | .. |
| German silver . ..... | 50 | 19 | .. | 13 |

NOTE: Great care must be exercised in adding the zinc and tin to the molten copper, to avoid oxidation of the two former, as much as possible.

EXPERIMENT No. 53: TESTS FOR COPPER IN SOLUTION. (a) To a small amount of copper sulphate solution in a t. t. add sodium or potassium hydrate—note change. Write reaction.

(b) To another add ammonia, or its carbonate—note change.

(c) To another add potassium ferrocyanide—note change.

(d) To another add potassium ferricyanide—note change.

EXPERIMENT No. 54: DEPOSITION OF COPPER. Clean your knife blade thoroughly with fine sand paper, or otherwise, and immerse in a solution of copper sulphate—note changes.

EXPERIMENT No. 55: In a test tube containing a small amount of copper sulphate in solution, place a small piece of zinc. Note changes.

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## PERIOD XIV

## METALLURGY OF COPPER—CONT'D

APPARATUS: Tumbler, zinc plate, copper plate, copper wire, crystallization dish, plaster cast wired, etc.

REAGENTS: Solution copper sulphate, tin foil, potassium bitartrate.

EXPERIMENT No. 56: DEPOSITION OF COPPER: THE CELL. Make a voltaic cell or battery by submerging in a glass tumbler sufficiently full of copper sulphate solution, a piece of copper plate with conductor passing from it, and over it a piece of zinc, with conductor passing from it.

EXPERIMENT No. 57: DEPOSITION OF COPPER: THE BATH. Make a deposition bath of glass crystallizing dish (or other apparatus) and fill with strong solution of copper sulphate.

EXPERIMENT No. 58: DEPOSITION OF COPPER: BASE. Attach to the negative conductor, which passes to the positive element zinc, the plaster cast properly prepared and wired. Then hang from the positive conductor, which arises from the negative element copper, the properly shaped anode of copper—submerge in the bath and set aside. On the cast will be slowly deposited a copper base, which remove, tin as directed in experiment 33, under Period IX, on "Tin", and use as base for vulcanization.

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## PERIOD XV
## METALLURGY OF IRON

APPARATUS: Tripod, sand bath, soldering pliers, sandpaper, Bunsen burner, tumbler, test tube, old burs.

REAGENTS: Ferrous sulphate, ferric chloride, ammonium sulphide, ammonium hydrate, potassium ferricyanide, potassium ferrocyanide, potassium sulphocyanate.

EXPERIMENT No. 59: HARDENING AND TEMPERING. Take eight old burs and heat to cherry red and plunge quickly into cold water, thus making them full hard. Polish with fine sandpaper, and heat again, one at a time, on sand bath which should be inverted and placed on tripod over the flame. (Use great care not to burn bench). As soon as the desired color is reached, roll the bur off into a glass of cool water. Prepare the eight different degrees of hardness as per table, page 228, text.

NOTE: If they are made too soft in tempering, or desired color is not obtained polish and again temper until proper color is reached.

EXPERIMENT No. 60. TEST FOR IRON IN SOLUTION. To small amounts of ferrous sulphate in a t.t. add ammonium

sulphide, potassium ferricyanide, ammonium hydrate. Note action, if any.

To small amounts of ferric chloride in a t. t. add potassium ferrocyanide, potassium sulphocyanate. Note action, if any.

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## PERIOD XVI

## METALLURGY OF ALUMINUM

APPARATUS: Test tubes.

REAGENTS: Sulphuric acid, nitric acid, hydrochloric acid, hydrogen sulphide, ammonium sulphide, ammonium hydrate, ammonium chloride, aluminum chloride, aluminum, zinc.

EXPERIMENT No. 61: ACTION OF THE ACIDS ON ALUMINUM. To small pieces of aluminum in separate t. ts., add the following: To the first, 1 c. c. of sulphuric acid; to the second, 1 c. c. of nitric acid; to the third, 1 c. c. of hydrochloric acid. Save for experiment No. 65.

EXPERIMENT No. 62: TEST FOR ALUMINUM SALT IN SOLUTION. To small amounts of aluminum salt (preferably the chloride) solution in t. ts., add the following reagent drop by drop: Hydrogen sulphide, ammonium sulphide, ammonium hydrate, of the latter add a slight excess. Compare with your notes on zinc tests.

EXPERIMENT No. 63: Prepare a little zinc chloride by adding a small amount of dilute hydrochloric acid to a piece of zinc in a test tube.

EXPERIMENT No. 64: To a c. c. of the zinc chloride solution in a t. t. and to a c. c. of aluminum chloride solution in a t. t., add to each, first a small quantity of ammonium chloride solution, and then about 2 c. c. of ammonium hydrate.

EXPERIMENT No. 65: Test the solutions made from acids in experiment No. 61 for presence of aluminum in solution. (See experiment No. 62.)

EXPERIMENT No. 66: Students will prepare one of the following alloys, as directed by the Instructor.

| ALLOY | Aluminum | Copper | Gold | Silver |
|---|---|---|---|---|
| Nürnberg gold | 7.5 | 90 | 2.5 | .. |
| Aluminum silver | 7.5 | .. | .. | 2.5 |
| Bronze | 10 | 90 | .. | .. |

NOTE: Each student must provide about 1 gm. of vulcanite filings for next period.

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## PERIOD XVII

## METALLURGY OF MERCURY

APPARATUS: Test tubes.

REAGENTS: Acetic acid, hydrochloric acid, sulphuric acid, nitric acid, hydrogen sulphide, potassium hydrate, ammonium hydrate, potassium iodide, mercur*ic* chloride, mercur*ous* nitrate, mercury, copper, lead, bismuth, tin, vulcanite filings.

EXPERIMENT No. 68: TEST FOR THE PRESENCE OF OTHER METALS IN MERCURY. To a t. t. containing a globule of mercury, add a small piece of lead foil and gently warm to readily amalgamate the two metals, then add equal parts of acetic acid and water, shake thoroughly and add a few drops of potassium iodide. Note change, if any.

EXPERIMENT No. 69: To a globule of mercury containing a little bismuth, add strong nitric acid, shake thoroughly, and add distilled water in excess. Note action, if any.

EXPERIMENT No. 70: To a globule of mercury containing a small piece of tin foil, add dilute nitric acid. Note change, if any.

EXPERIMENT No. 71: To small amounts of red vulcanite filings in separate t. ts. add the following: Dilute nitric acid, sulphuric acid, hydrochloric acid. Save for experiment No. 73.

EXPERIMENT No. 72: To a small amount of mercur*ic* salt solution in a t. t. add the following: Hydrogen sulphide, potassium hydrate, ammonium hydrate, potassium iodide. To a small amount of mercur*ous* salt solution in a t. t. add the following: Hydrogen sulphide, hydrochloric acid, potassium iodide, potassium hydrate, ammonium hydrate.

EXPERIMENT No. 73: Test the solutions from experiment No. 71 for mercury in solution.

EXPERIMENT No. 74: DEPOSITION OF MERCURY. Into a test tube containing a little mercuric chloride, slightly acidulated with hydrochloric acid, introduce a small strip of clean copper foil.

NOTE: Each student will provide himself with a silver dime for next period or the equivalent amount of silver and copper.

# PERIOD XVIII
# METALLURGY OF SILVER

APPARATUS: Florence flask, sand bath, tripod, Bunsen burner, evaporating dish, funnel, filter paper, beaker, test tubes, silver dime.

REAGENTS: Nitric acid, sodium hydrate, sodium chloride, hydrochloric acid, potassium chromate, hydrogen sulphide, potassium cyanide.

EXPERIMENT No. 75: REFINING SILVER. Place a silver dime in a Florence flask, add about 20 c. c. of nitric acid, and dilute the acid with the same amount (20 c. c.) of distilled water. Gently warm the whole on a sand bath to hasten action.

EXPERIMENT No. 76: PREPARATION OF SILVER NITRATE CRYSTALS. When the dime or alloy of silon and copper has dissolved, place 4 or 5 c. c. of the solution in an evaporating dish and evaporate at a gentle heat. (The solution remaining in the flask should be tightly stopped and placed in a locker in Metallurgic Laboratory for next period.) After the water of solution and free acid is driven off, the evaporating dish will contain a greenish solid of silver and copper nitrates. By continued heat and stirring the silver nitrate is fused and the copper nitrate changed to copper oxide by the disengagement of nitrogen dioxide. When *all* the green copper nitrate has been changed to the black oxide of copper and the dish has *cooled* sufficiently to be handled, add a small quantity of distilled water, about 20 c. c., stir well and filter. Silver nitrate is soluble in water and therefore passes through, while the black insoluble cupric oxide is left on the filter paper. Save about 5 c. c. for experiment No. 77. Cleanse the evaporating dish thoroughly, rinsing with distilled water, place the remaining silver nitrate solution in it, and evaporate to crystals, at a low heat.

EXPERIMENT No. 77: TEST FOR SILVER SALTS IN SOLUTION. To a small quantity of silver nitrate in a t. t. diluted with an equal amount of *distilled* water add the following reagents, noting action, if any; sodium chloride, hydrochloric acid, sodium hydrate, potassium chromate, hydrogen sulphide. (Save a little silver sulphide for experiment No. 78.)

EXPERIMENT No. 78: Divide silver sulphide prepared in the above experiment, into two parts. To one, add moderately

concentrated nitric acid (distinction from mercury), to the other add potassium cyanide (distinction from copper.)

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## PERIOD XIX

## METALLURGY OF SILVER—CONT'D

APPARATUS: Florence flask, flint bottle, beaker, stirring rod, crucible, nails.

REAGENTS: Sulphuric acid, sodium chloride, ammonium hydrate, potassium carbonate, borax.

EXPERIMENT No. 79: Pour the silver nitrate and copper nitrate solutions contained in the Florence flask, used at last period, into a large beaker, and add a saturated solution of sodium chloride until no more silver chloride is formed. Transfer to clean flask and shake for several minutes, then allow the ppt. to settle. A little more sodium chloride added will determine whether all the silver has been thrown down. Decant the supernatant liquor. The chloride must now be washed several times, the water decanted off each time after the white ppt. has settled. By repeated washings the copper nitrate is removed, being soluble the presence of merest trace is indicated by a blue tinge on the addition of ammonium hydrate. When *entirely free* from copper, the silver chloride should be placed in a large flint bottle, with twice its bulk of water added, to which a sufficient amount of sulphuric acid is then added to warm the whole, slightly. Twenty small nails or pieces of iron are now added to contents of bottle; stir the mixture with a glass rod until every particle of the mass becomes dark gray, showing that the chlorine has been disengaged and the silver is free. The failure to break up any portion of the chloride, will result in a loss of silver. Remove *all* of the nails, counting them to be sure, wash several times, with water, dry, mix with an equal amount of potassium carbonate, and melt in a well boraxed crucible.

NOTE: Students will provide for the next period old gold scraps, fillings, crowns, or jewelry of any kind in sufficient quantity to produce when refined about 2½ dwts. of pure gold.

## PERIOD XX
## GOLD

APPARATUS: Balances, crucible.

REAGENTS: Borax, potassium carbonate, potassium nitrate, ammonium chloride, charcoal gold scraps.

The Instructor must see all gold or alloy scraps before it is melted.

EXPERIMENT No. 80: Weigh the gold or alloy scraps *very accurately* before proceeding, and make a note of the weight and character of the scraps.

ROASTING PROCESS: Roast the alloy scraps (which should be brittle if simply melted, on account of a base metal content), for twenty minutes to half an hour, in a well-boraxed crucible with potassium nitrate. If the metal is in small pieces or filings, it should be covered with potassium carbonate. During the roasting, potassium nitrate should be added from time to time to the molten metal in small pieces, or the metal may be lost in the ebullient overflow of flux from the crucible. A little borax should also be added from time to time, as it, too, unites with oxides of the base metals and assists in their removal. Pour the contents of the crucible, after roasting, into a well-oiled and warm ingot mold and *compare with first weight.* If malleable, roll to ribbon, 30-gauge.

If the alloy is brittle and can not be rolled, it should be roasted a second time, with ammonium chloride and powdered charcoal. Such roasting must be continued until the gold is malleable.

NOTE: Be sure and weigh the metals before and after each roasting, noting loss, if any, and account for any loss that may have occurred, also state the flux used during the roasting.

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## PERIOD XXI
## GOLD—CONT'D

APPARATUS: Balances, flask, Bunsen burner, crucible.

REAGENTS: Nitric acid, sulphuric acid, gold alloy, silver borax.

EXPERIMENT No. 81: PARTING GOLD: Alloy not less than two and a half pennyweights (2½ dwts.) of gold alloy, made malleable during Period XX with three times its weight of coin or fine silver, roll the alloy into a thin ribbon, about number 35-gauge; cut the ribbon in very small pieces and carefully place in a Florence flask, then add about one and a half ounces of either nitric acid or two and one-half ounces of sulphuric acid. Heat until no more fumes are given off. Decant off the liquid and save; add about an ounce of fresh acid and continue the process. Decant the acid. Wash the contents of the flask thoroughly in hot water, to remove the nitrates or sulphates of the contaminating metals. The silver of the decanted liquor can be saved as per Period XIX.

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## PERIOD XXII

## GOLD—CONT'D

APPARATUS: Evaporating dish, Florence flask, sand bath, Bunsen burner, filter, funnel, ring stand.

REAGENTS: Gold, nitric acid, hydrochloric acid, ferrous sulphate, oxalic acid.

EXPERIMENT No. 82: CHEMICALLY PURE GOLD. After the gold resulting from the parting process is thoroughly washed, place it in an evaporating dish, pour on about 40 c. c. of hydrochloric acid and about 10 c. c. of nitric acid. Warm gently on sand bath. If this quantity is not sufficient to dissolve the gold, add more aqua regia in above proportions. The solution must now be evaporated down at a very gentle heat (lest gold chloride be reduced) to about two-thirds its original bulk.

A white ppt. will be noticed in the dish, which is the chloride of silver. Decant off the gold to second evaporating dish, leaving the chloride of silver in the first. Add hydrochloric acid to decompose the last of the nitric acid and further evaporate the gold solution, to the consistence of syrup, and of a deep orange-red color.

The solution may now be allowed to cool, the dish filled with distilled water and placed with contents in a funnel and filter paper. Wash all the gold chloride through the filter, by the use of a wash bottle, into a Florence flask.

The gold may now be precipitated by adding a saturated solution of either ferrous sulphate or oxalic acid, slightly warming on a sand bath for ten or fifteen minutes. It should then be placed in the locker in the Metallurgic Laboratory until next period.

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## PERIOD XXIII
## GOLD—CONT'D

APPARATUS: Funnel, filter, ring stand, tripod, evaporating dish, crucible, beaker.

REAGENTS: Hydrochloric acid, ferrous sulphate, potassium bicarbonate, potassium carbonate, potassium nitrate.

EXPERIMENT No. 83: CHEMICALLY PURE GOLD. A small amount of the precipitant (ferrous sulphate) may now be added to determine if all the gold has been thrown down. If so, carefully decant off the supernatant liquid, wash the ppt. with dilute hydrochloric acid, then distilled water, then dilute ammonia, and again with distilled water. In case oxalic acid has been used as a precipitant, heat the gold in the flask over a sand bath with a weak solution of potassium carbonate. If ferrous sulphate has been used as the precipitant, warm the hydrochloric acid solution used above, to get rid of any iron. Wash the gold into an evaporating dish. In the form precipitated, of powder scales, or foil, the gold is to be dried and placed in a well-boraxed crucible, covered with a little potassium carbonate and fused with a little potassium nitrate, cooled in the crucible, or poured into a clean and well-oiled ingot mold, then washed with hydrochloric acid, rolled, and finally part of it further rolled out between pure filter papers, to a number 30 foil for filling, and used in the infirmary for at least one gold filling.*

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## PERIOD XXIV.
## AMALGAM ALLOYS

APPARATUS: Crucible, balances, ingot molds, glass-tubing.

*By covering the surface of gold or platinum foil with oil, it can be folded upon itself and rolled much thinner than the usual way. Boil in a solution of KOH, and wash with dilute HCl and water after rolling.

REAGENTS: Borax, silver, gold, platinum, tin, copper, zinc, antimony, cadmium.

EXPERIMENT No. 84: Each student will select one of the alloys on pages 364 and 365 of the text, and prepare it as accurately as possible according to the formula there given. It will not be necessary to make more than ten pennyweights of the alloy. Inasmuch as the formulas are all given in hundredths, the preparation of ten pennyweights will express the formula in tenths.

The student will carefully write the formula he desires to make, at the top of the page of his note book, being very careful to state the exact proportions and the sum of the weights of the various metals entering into the formula. Great care must be exercised in accurately weighing each metal, and in melting them together, so as to avoid any loss, if possible. Use only clean, well-boraxed crucibles; warm, well-oiled and clean ingot molds. After melting and pouring into ingot molds, clean up the ingot thoroughly, accurately weigh and note the comparison of the weight before and after melting.

Before the next period the ingot of dental-amalgam alloy must be comminuted and presented to the Instructor for inspection and tests for its various properties.

## PERIOD XXV

APPARATUS: Bunsen burner, funnel, filter paper, test tube, beaker, evaporating dish.

REAGENTS: Hydrogen sulphide, hydrochloric acid, nitric acid, sulphuric acid.

Follow closely "Analysis of Dental-Amalgams" on page 394 text.

EXPERIMENT No. 85: Make a qualitative analysis of 2 grams of old amalgam fillings.

EXPERIMENT No. 86: While carrying on Experiment No. 85, make a quantitative analysis of the silver in the amalgam filling which is being examined.

## WORK TO BE HANDED IN

All work must be passed in to the Professor of Chemistry and

Metallurgy, thirty days before the end of the term. Each piece must have the stamp of the Instructor, or a certificate from him, indicating that the work was done in the Laboratory at regular hours, and by the student or students presenting it.

ALL INGOTS OF ALLOYS prepared in the Laboratory must be nicely polished, measure accurately 5x10x40 mm., and bear the formula, weight before and after melting neatly scratched on one of the 10x40 sides.

A BASE, either cast, swaged, or deposited; if cast or swaged, the alloy must have been prepared in the Laboratory.

A FILLING of gold foil prepared in the Laboratory must be inserted either in an extracted tooth or a tooth *in situ*. If in an extracted one, part of the filling is to present a finished surface and part unfinished, with a small piece (at least ½ inch) of the foil attached.

ORIGINAL and unrequired work will be deservedly credited.

## LABORATORY REAGENTS

| Left-hand end. | Right-hand end. |
|---|---|
| Ammonium Hydrate | Sulphuric Acid |
| Sulphuric Acid | Nitric Acid |
| Nitric Acid | Hydrochloric Acid |
| Hydrochloric Acid | Acetic Acid |
| Acetic Acid | Oxalic Acid |
| Oxalic Acid | Calcium Chloride |
| Calcium Chloride | Ammonium Chloride |
| Ammonium Chloride | Barium Chloride |
| Barium Chloride | Platinic Chloride |
| Platinic Chloride | Ferric Chloride |
| Ferric Chloride | Potassium Iodide |
| Potassium Iodide | Calcium Sulphate |
| Calcium Sulphate | Potassium Sulphate |
| Potassium Sulphate | Ferrous Sulphate |
| Ferrous Sulphate | Magnesium Sulphate |
| Magnesium Sulphate | Copper Sulphate |
| Copper Sulphate | Lead Acetate |
| Lead Acetate | Potassium Ferrocyanide |
| Potassium Ferrocyanide | Potassium Sulphocyanide |
| Potassium Sulphocyanide | Potassium Ferricyanide |

| | |
|---|---|
| Potassium Ferricyanide | Alcohol |
| Alcohol | Hydrogen Sulphide |
| Hydrogen Sulphide | Ammonium Sulphide |
| Ammonium Sulphide | Disodium Hydric Phosphate |
| Disodium Hydric Phosphate | Ammonium Oxalate |
| Ammonium Oxalate | Silver Nitrate |
| Silver Nitrate | Sodium Carbonate |
| Sodium Carbonate | Ammonium Carbonate |
| Ammonium Carbonate | Calcium Hydrate |
| Calcium Hydrate | Sodium Hydrate |
| Sodium Hydrate | Potassium Hydrate |
| Potassium Hydrate | Ammonium Hydrate |
| Ammonium Hydrate | Blank |
| Blank | Blank |
| Blank | Sulphuric Acid |
| Ammonium Sulphocyanide | Nitric Acid |
| Space | Hydrochloric Acid |

## RULES AND SUGGESTIONS TO STUDENTS

I. Begin your work by placing on the bench in front of you, your towel, such apparatus as you need for the exps., and your note book. Prepare for doing the first exp. of the day, and read it entirely through before attempting to perform any part of it.

II. Before every laboratory exercise you should make a thorough preparation for the experiments by studying several textbooks on the subject.

III. Each student must be provided *with a cloth to keep the bench clean* and something to protect the clothing from injury while at work.

IV. The bench at which you work must be left *clean* and *dry* after every laboratory exercise. *Carefully wipe* off a ring stand, *burner,* or other *apparatus* on which a reagent has fallen, wipe out a p. t. after using it, and *keep reagent bottles, apparatus, books and lockers clean.* Iron and steel objects must not be put away wet, or they will rust. Any substance dropped on the *floor* must be *brushed* or *wiped up.*

V. In experimenting, *follow the directions as closely as possible,* and ask an *explanation* of anything *not understood.* Have your apparatus *neatly arranged* without artificial props, wedges, or uncouth-looking materials. *All apparatus and chemicals must be clean and pure.*

VI. Have every d. t. and stopper a close fit, to prevent leakage of gas. If a gas generates well but does not pass into the rec., there is some leakage, due probably to loose bearings. Old stoppers will scarcely ever do to use. *Rubber stoppers* may be used for a long time, but should be *detached after every exercise.* Before any tube

is put into a stopper, make sure that it has been *properly rounded.* To put a tube into a rubber stopper, moisten both the tube and the hole in the stopper. To put a stopper into a t. t., clasp the latter near its mouth with the left hand and gently press in the stopper with the right, keeping it perfectly straight, so as not to break the glass.

VII. In heating a t. t. on a r. s., hold the *burner* in the hand, move it slowly, and now and then take it away from the tube for a few seconds after the action has become vigorous, or the tube may melt or break.

VIII. In heating a substance in an e. d. or a flask, have the latter usually not more than 5 or 10 cm. above the top of the *burner,* unless it is desired to heat slowly. If the ring which holds the plate can not be easily lowered to that distance, put a small ring below on which to rest the *burner,* but do not raise the *burner* with books placed underneath.

IX. *Mixtures of solids should be made on paper,* and thence carefully poured into the receptacle. You should have in your *locker old newspapers,* etc., neatly cut about the size of the leaves of this book. *Use filter papers for nothing but filtering. Small splints* should be used for testing combustion. *Be careful not to mix chemicals or reagents, whether solids or liquids, except as directed.*

X. *Never put down a glass stopper,* when using a reagent bottle, if you can avoid it, but hold it between the first and second fingers, and replace it when you put down the bottle. *Do not pour back any excess* of a reagent from a t. t., or rec. into a reagent bottle, and *do not dip a s. r. or pipette* into a reagent bottle. In reddening litmus paper for use, never dip it into an acid, but hold it in the *fumes* of HCl. To turn it blue, use the fumes of $H_3N$.

XI. In pouring a liquid into a t. t. or graduate, hold the latter on a level with the eye, towards the light, and in such a way as not to conceal the substance already therein, but so as to see any phenomena.

XII. Pour only liquids, fine solids, or soluble salts into the sinks, *always opening the faucet first to let the water run,* other solids should be thrown into the jars. *Great care must be taken not to clog the discharge pipes with glass, matches or other solids.*

XIII. *Wipe your flask, e. d., or tube* perfectly dry on the outside *before applying heat.* Tubes of thick glass, if they contain no liquid, should be heated gradually by moving them rapidly into and out of the flame. When once heated, they may be held steadily in the flame. If a hot flask or tube holds a liquid, it is not injured by pouring water on the outside, but if it contains only a solid, or is empty, it should be cooled till it can be handled, or water will break it.

XIV. The hottest part of a Bunsen flame is about half way up, just above the inner cone. Substances to be strongly heated should be held there.

XV. *On leaving the laboratory be sure that everything is put back in place, the part of the bench you have occupied wiped clean and dry, and the locker locked.* Reagents for general use must not be taken to the individual's bench, but left where they belong, and *nothing must be put into your locker except what belongs there.*

XVI. Endeavor to carry away from each exp. a mental picture of the apparatus as it is set up, of the colors and appearance of the substances used, and of the products obtained—whether they are solids, liquids or gases, in solution or not, crystalline or amorphous, etc. In recalling and describing exps. state all of these, together with the names and symbols of the factors and products,

but *do not try to recall quantities of substances used.* By noting and comparing the colors and odors of gases, many substances can be recognized. To take the odor of a noxious gas, waft some of the gas with the hand from the mouth of the tube or rec. to the nose, thus diluting it.

XVII. Write your name and locker number distinctly across the front of your notebook, also write your name, locker number, subject of the exp. and date, at the head of each perforated page. Be sure the black sheet is properly placed to copy it on the page beneath. When the page is filled, number it, tear it out carefully, and at the finish of the work, place all removed pages in drop-box provided. No notes should be made outside of the laboratory without special permission. Take your notebook with you at the end of the hour, and study the exps. for recitation. Leave the black sheet in your locker.

XVIII. It is of the greatest importance that you should see all there is in an exp., and the order in which changes take place, and state your observations *briefly* and in *correct English.* Your notes should embody the following points—(1) *Chemicals* (*names* and *symbols*), *apparatus* and *adjustment* (*very briefly* and *not copied from the directions*). (2) *Observations* and *results* (*such as whether solid, liquid, or gaseous,* the *color, odor, increase of temperature or of volume, effervescent action, precipitation, sublimation, etc.* (3) *Explanation of each change* (i. e., what it indicates to you, or how chemists account for the phenomena, together with a reaction where this is possible). *Put the main stress on* (*2*) and (*3*). Try to distinguish in an exp. what you see that is important from what is not so, and whenever you give an explanation think *whether the exp.*

*teaches it, or whether you have got it from some outside source.* Write each reaction on a line by itself immediately following the explanation it is intended to complete. Indicate gases in a reaction by an arrow, above and to the right of the symbol, as $H_3N\nearrow$, and ppts. by a brace underneath, as $\underbrace{PbSO_4}$. Record of an exp. must be made on the spot, either as soon as the exp. is completed, or often before it is done, at a convenient place for a pause. For valences, symbols, names, solubilities, etc., of substances, refer to charts; if they are not there, consult the instructor.

ABBREVIATIONS.

| | | | |
|---|---|---|---|
| app. | apparatus. | ppt. | precipitate. |
| b. | beaker. | p. t. | pneumatic tube. |
| c.c. | cubic centimeters. | qcm. | square centimeters. |
| cm. | centimeters. | reagt. | reagent. |
| cpd. | compound. | rec. | receiver (wide-mouth bottle.) |
| dil. | dilute. | r. s. | ring stand. |
| dis. | dissolve. | sat. | saturate. |
| d. t. | delivery tube. | soln. | solution. |
| e. d. | evaporating dish. | sp. gr. | specific gravity. |
| Exp. | experiment. | s. r. | stirring rod. |
| f. f. | Florence flask. | t. t. | test tube. |
| Gm. | grams. | vol. | volume. |
| gen. | generator. | | |
| insol. | insoluble. | | |
| i. t. | ignition tube. | | |
| m. s. | metric system. | | |
| N. T. P. | normal temperature and pressure (0°, 760 mm.) | | |

Rules, with slight alterations, from *Laboratory Manual.*—WILLIAMS.

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